

THERMODYNAMICS

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BY

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NEW YORK

JOHN WILEY & SONS, INC.

LONDON: CHAPMAN & HALL, LIMITED

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THIRTEENTH PRINTING, AUGUST, 1957

PRINTED IN THE UNITED STATES OF AMERICA

TO MY WIFE
ISABEL MORRISON KEENAN

PREFACE

The object of this book is to give a simple and rigorous exposition of the First and Second Laws of thermodynamics. Work, temperature, and heat are explicitly defined. The First Law is stated in terms of work and heat alone. The term energy — which represents a thermodynamic concept — is quantitatively defined. Without employing molecular pictures that hold only for idealized gases, internal energy is shown to be a property. Steady flow is approached through the more general concept of the open system..

Illustrative material, particularly in the first eight chapters, is drawn from familiar things and processes, including familiar chemical reactions. Consequently, the treatment is kept general and relatively free from algebraic manipulation.

The Second Law appears as a single statement, and the usual equivalent statements are derived as corollaries. The concept of reversibility is rigorously defined; it is then applied to familiar processes through examples and problems. The entropy is shown to be a property, but the distinction between entropy and the heat-temperature quotient is emphasized by a derivation of the Clausius inequality and by frequent application of it.

The chapter on availability appears as a logical extension of principles that are applied in previous chapters — notably those on corollaries of the Second Law, introduction to thermodynamics of chemistry, and heat and power from combustion. Hitherto unpublished examples are given of the application of the availability principle to the ammonia-absorption cycle and the internal-combustion-engine process. A quantitative definition of irreversibility is offered.

The material in the chapters on the relation between pressure, volume, and temperature and on binary mixtures is not new to the chemical engineer. To the mechanical engineer it is less familiar but equally important.

In the last few chapters the emphasis is on equilibrium. The treatment of this subject brings out the interrelation between equilibrium and work-producing processes. It presents that part of the work of Willard Gibbs which seems to bear most directly on problems in engineering. Moreover, it provides a broad and sound foundation for the discussion of equilibrium in the field of mechanics.

Although the emphasis is on thermodynamics rather than on heat engineering, adequate treatment is given of engines, cycles, refrigeration, air conditioning, and other subjects that are usually included in a course in heat engineering. Each of these subjects serves to illustrate some phase of the application of the First and Second Laws to science and engineering.

No one arrangement of material would be satisfactory to all teachers of the subject for all courses of study. However, the following approach has been tested in practice and may serve as a guide in planning a program.

The first term may be devoted to Chapters I to IX. The order of these chapters is important if the method of exposition is to be used to best effect. The second term may include some or all of Chapters X to XVI. Here the order is of less importance and some topics, such as the treatment of partial properties in Chapter XIV, may if necessary be postponed. Further undergraduate work may be selected from Chapters XVII to XXII. Topics for graduate study may be selected from Chapters XXIII to XXVI. No student, graduate or undergraduate, should be expected to master an advanced chapter until he is thoroughly familiar with the methods and contents of Chapters I to IX.

Most of the material in the first half of the book has taken shape over a period of years through successive revisions of a text in mimeograph. This material has been used by instructors of various degrees of experience to teach students of several branches of engineering. Although still subject to improvement, the method of exposition is no longer in an experimental stage. It has been used successfully with both graduate and undergraduate students.

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CAMBRIDGE, MASS.

September, 1941

ACKNOWLEDGMENTS

It is a pleasure to acknowledge my indebtedness to the many colleagues, friends, and teachers who have helped me to write this book. Only a few can be mentioned here.

Professor Charles W. Berry was my first teacher in thermodynamics. Doctor Harvey N. Davis, who introduced me to the study of the properties of vapors, has generously shared with me his broad experience as a teacher. Professor Frederick G. Keyes has kept me informed of methods and progress in thermodynamic research.

In the study of equilibrium through the works of Willard Gibbs I was tutored by the late Professor Louis J. Gillespie. Professor James A. Beattie helped to clarify my concepts of the elements of the subject. He generously made room in his crowded program for a survey of the chapters on temperature and equilibrium.

In 1912 Professor Henry B. Phillips prepared classroom notes containing proofs of the Clausius inequality, the principle of the increase of entropy, and the proposition that entropy is a property. I have found no published proofs comparable to these in rigor, simplicity, and economy. Through the kindness of Professor Phillips I have borrowed from them in Chapter VIII.

The discussion of the equation of state for mixtures in Chapter XX was guided largely by material in *Thermodynamics for Chemical Engineers* by my colleague Professor Harold C. Weber. Mr. Ascher Shapiro contributed to Chapter XIII, and Mr. Lloyd T. Andrew to Chapter IX. Professor Thomas K. Sherwood provided the data for the ammonia-absorption cycle analyzed in Chapters XV and XVII. Doctor Joseph Kaye read the entire manuscript and rendered many other services. My wife labored long and patiently over manuscript and proof.

J. H. K.

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CHAPTER I

DEFINITIONS

Thermodynamics. Thermodynamics is the science of the relationship between heat, work, and the properties of systems.

System. A system is any collection of matter enclosed within prescribed boundaries.

Pressure. The force exerted by a system on unit area of its boundaries (and, therefore, by unit area of the boundaries on the system) is called the pressure of the system. Where the pressure is continuously varying it must be defined as the force applied by the system on an infinitesimal piece of the boundary divided by the area of the piece. Usually the force applied by the system is directed outwards, and the pressure is considered positive. Occasionally a system in a solid or a liquid state will apply a force on its boundaries which is directed inward — the pressure is then considered negative.

Specific Volume and Density. The volume occupied by unit mass of a system is called its *specific volume*. Where the specific volume is varying from point to point in a system it must be defined as the volume occupied by an infinitesimal fraction of the system divided by the mass of the fraction. The specific volume is the reciprocal of the *density*.

Work. The definition of work used in mechanics is “the product of a force and the distance in the direction of the force over which it is applied.”

When a piece of chalk is lifted from a table to the top of a box resting on the table, work is done by the agent which does the lifting. If we consider a system consisting of the table, the chalk, and the box it is apparent that the configuration of the things constituting the system is changed by the work. We may say that the introduction of work into the system results in a change in state, where the word *state* is used to denote the configuration of the system.

Work is present only during the action of the agent. Before the action no work is present; and after the action no work is present. The work appears only during the change of state and is something which enters the system from outside. Its existence is fleeting. The transitory nature of work is one of its distinguishing characteristics.

Work is characterized by another distinguishing feature: it is always

equivalent to and can be completely converted into the raising of a weight. Regardless of the direction in which the force acts, by a suitable system of pulleys or levers an equivalent force acting over the same distance can be made to raise a weight. If care is taken to reduce friction in the mechanism, the magnitude of the mass which can be raised through a prescribed change in level by a given amount of work can be made to approach indefinitely close to a certain maximum value. We shall use that maximum value as a measure of work.

In thermodynamics *work* is defined as follows: *Work flows from a system (and to another) during a given operation if the sole effect external to the system could be the rise of a weight.* It is measured by the magnitude of the greatest weight which could be lifted through a prescribed distance. Our definition includes not only the work defined in mechanics but certain other kinds of transitory quantities as well.

To illustrate another kind of work consider a system in a state of stable equilibrium (that is, a state which will not alter in the absence of external effects) which has a potential difference E between two points on its boundaries. If a quantity of *positive electricity* dZ is caused to flow out of the system at the point of higher potential and into it at the other point a change will occur in some observable characteristics of the system. For example, if the system is a capacitor, there will be a change in the deflection of a galvanometer connected across it; or if the system is a lead storage cell, there will be a change in the mass of the electrodes and in the composition of the electrolyte. These changes are the result of the flow of electricity through the potential difference.

We learn from the science of electricity that the sole external effect of this flow of electricity could have been the rise of a weight. For, if the electricity were to flow from the part of the system at high potential to a motor, and from the motor to the part of the system at low potential, the motor could raise a weight. Moreover, if the resistances of the motor were reduced indefinitely the number of pounds of mass that would in the limit be raised through a height of one foot bears the same relation to the product EdZ that the joule bears to the foot-pound. In the limit, also, no effect other than the rise of the weight would be observed outside the system. Thus, in the thermodynamic sense, the system has delivered work.

It can be said further that whatever things external to the system this flow of electricity passes through will receive the work.

A similar argument may be used to show that work may be transferred to or from a paramagnetic substance by changing its magnetization in a magnetic field.

The first type of work, the mechanical type, will be used to illustrate

most of the simpler parts of our subject. It is virtually the only kind of work which can be conveniently delivered in any appreciable quantity to gaseous systems.

Work flowing from a system we shall call positive work, and work flowing to a system we shall call negative work. For example, consider a helical spring which is stretched in the direction of its axis. If the spring contracts slowly against an external resistance, then we shall say that the work done by the spring is positive, because the spring could execute the same operation and leave no external effect except the rise of a weight. On the other hand, if the spring is stretched slowly then we say that work is done on the spring or that the work done by the spring is negative. For, the operation of the agent that stretched the spring was such that the sole effect external to the agent could have been the rise of a weight. Therefore the agent delivered work and the spring received it.

Work is measured by the magnitude of the greatest weight which could be lifted through a prescribed difference in level. It can be shown from the principles of statics that if two forces, F_1 and F_2 , move respectively through distances s_1 and s_2 in the direction of the forces, then the work done by force F_1 is n times the work done by force F_2 if

$$F_1 s_1 = n F_2 s_2.$$

Therefore, *work done by a force may be measured by the product of the force and the distance it moves in its own direction*. Thus, we may write an expression for the work done by a force:

$$dW_F = F ds,$$

where dW_F denotes the work done by force F as it moves a distance ds in its own direction.

Temperature. Suppose that we have two pieces of the same material, one of which feels hot to the touch and the other cold. If we place them in contact with each other we soon notice a change in both, the first feels less hot, the second less cold; and after a considerable period of time has elapsed we find that both feel the same.

The same phenomenon might have been observed in a less subjective fashion. Suppose, for instance, that the two masses in question are blocks of copper. If a deep hole is drilled in each we can insert in the hole a glass bulb filled with mercury the surface of which stands somewhere in a capillary extension of the bulb. (This device is known as a mercury-in-glass thermometer.) If we insert the mercury bulb into each of the blocks before bringing them in contact we find that the level of the mercury surface is higher when the bulb is in the hot block than when it is in the cold block. After the two blocks have been in contact with

each other for a long time the mercury level will be the same with the bulb in either block. The two blocks are now said to be at the same temperature.

More detailed observation would reveal that the length of a side of the hot block decreased and the length of a side of the cold block increased during this experiment, or that the electrical resistance of the first had decreased and that of the second had increased, but after a considerable period of time has elapsed no changes in length or resistance occur as long as the two blocks remain isolated from everything but each other. We define *equality of temperature* as that condition of two or more bodies in which no change in any observable characteristic occurs when they are brought into communication with each other.

The mercury in our mercury-in-glass thermometer is merely a body which executes a readily observable change in volume when it is brought into communication with a body that is not equal to it in temperature. Consider now a thermometer and two other bodies. If the volume of the mercury remains unchanged when it is brought into communication with one of the bodies, then the body and the thermometer are equal in temperature. If the volume of the mercury remains unchanged when the thermometer is brought into communication with the second body, then we know from experience that no change will occur in either of the two bodies if they are brought into communication with each other. We may say, therefore, that *if two bodies are each equal in temperature to a third body they are equal in temperature to each other*. If this were not so, equilibrium would never subsist within a group of bodies.

We can distinguish various levels of temperature now, because if a body is removed from one isolated group and brought in contact with a body from a second isolated group then the two groups are at different levels of temperature if a change occurs in an observable characteristic of one or both of the bodies which are brought together. Of course a simple way to carry out this investigation would be to include our indicator, the mercury bulb and stem, in one group of bodies and note whether the position of the meniscus changes when the indicator is brought in contact with a second group. It would be permissible in the absence of further concepts to say that of two groups of bodies the one which causes the mercury meniscus to come to rest at the higher position is at the higher temperature. A still more arbitrary, but equally permissible, step would be the definition of a scale of temperature by assigning numbers in sequence to marks placed at regular intervals along the capillary tube, the numbers being higher the farther the mark from the bulb, in accordance with our definition of a higher temperature.

In this manner the two most commonly used scales of temperature

were originally defined. On the Centigrade scale the number 0 was assigned to the mark corresponding to the temperature level of melting ice at atmospheric pressure and the number 100 to the mark corresponding to the temperature level of boiling water at the same pressure. On the Fahrenheit scale the corresponding levels were assigned the numbers 32 and 212 respectively. In each case the length of the stem was divided into equal intervals, so that a change of one in either scale was always denoted by the same distance.

Thermodynamics and Molecules. In hydraulics we are accustomed to conceive of the pressure of liquid water on the walls of its container as varying continuously from point to point, with no points on the submerged surface at which the pressure drops discontinuously to zero. On the other hand, the kinetic theory of matter teaches that pressure is caused by a bombardment of the walls of the container by myriads of discrete particles called molecules. Therefore, the pressure that we measure is continuous neither with distance nor with time; and our definition of pressure as the force applied at a given instant on an infinitesimal piece of boundary divided by the area of that piece will yield values which range at random from zero to infinity.

However, if the scale of our system is indefinitely large compared with molecular distances, an infinitesimal fraction of the boundary area might still be an extremely large area in terms of molecular distances. Our definition of pressure would then correspond to a finite and steady value. Similarly we may give meaning to the value of a temperature or of a density at a point provided that the point lies in a sufficiently large system.

Thus, thermodynamic analysis is limited to systems that are large compared with the molecules which they comprise. However, since a cubic centimeter of gas at room temperature and pressure contains about 3×10^{19} molecules, no very great dimensions are necessary to satisfy this requirement.

The existence of the molecule has been firmly established by experiment, but the science of thermodynamics does not depend upon this fact for its validity. Indeed, if it were to be proved tomorrow that the molecule is non-existent and all matter is continuous in nature, no change in the theory of thermodynamics need follow. In subsequent pages the molecule will play but a small part, because it is generally true that the exposition of thermodynamics is simplified by ignoring the molecule.

Heat. If we immerse 0.1 pound of copper having a temperature of 200 degrees on the Fahrenheit scale in a mass of 1 pound of water having a temperature of 60 degrees on the same scale the copper and the water will, after a time, reach equality of temperature. The new temperature

is found to be 61.4 degrees, or the water is raised in temperature 1.4 degrees by the copper. The results of this experiment may be reproduced at will; that is, 0.1 pound of copper at 200 degrees always raises the temperature of 1 pound of water 1.4 degrees (if the water is initially at 60 degrees) when the two are brought together. Consequently, 0.2 pound of copper will raise the temperature of 2 pounds of water 1.4 degrees (if the water is initially at 60 degrees), because we have merely combined two identical experiments.

In these experiments the copper has influenced the water in a fashion that can be quantitatively measured. The *influence* can be thought of as something which passed from the copper to the water, and it can be measured by the number of pounds of water which will rise through a prescribed interval of temperature as a result. It is called *heat*.

It was necessary, of course, to have a temperature difference between the copper and the water in the experiments just discussed or no measurable influence on the temperature of the water would have been found. It should be noted also that what is measured by the mass of the water which rises through the prescribed interval of temperature is that which *passed* from the copper to the water.

Heat is that which transfers from one system to a second system at lower temperature, by virtue of the temperature difference, when the two are brought into communication. It is measured by the mass of a prescribed material which can be raised in temperature from one prescribed level to another.

Heat, like work, is a transitory quantity; it is never contained in a body. The importance of this distinction will be made evident in later discussions.

We shall adopt the convention that *heat passing to a system is positive*, and heat leaving a system is negative.

State, Property, and Change of State. A *state* of a system is its condition or position and is identified through the properties of the system.

A *property* of a system is any observable characteristic of the system.

Two states of a system are called *identical states* if every property of the system is the same in both instances.

When the state of a system alters, the *change of state* is described in terms of the end states.

The *path* of a change of state is the series of states through which the system passes.

The *process* involved in a change of state is described in terms of the path and the method by which the path is described. An adequate description of the method must include at least the heat or the work.

Any process whose end states are identical is called a *cycle*.

Corollaries of these definitions follow:

All properties are identical for identical states.

The change in a property between any two prescribed states is independent of the process.

Any quantity whose change is fixed by the end states, i.e., is independent of the process, is a property. This is a rigorous criterion by which we shall hereafter determine whether a quantity is or is not a property.

PROBLEMS

1. A system consisting of a quantity of gas exerts a steady pressure of 20 lb/sq in. gage on a 10-in. diameter piston as the piston moves through 6 in. How much work is done by the system? (Assume a barometer of 29.92 in. of 32 F mercury.)

2. How many pounds weight will the following quantities of work raise through a height of 1 ft: 1000 ft-lb, 1000 kg-m, 1000 ft-poundals, 1 hp-hr, 6 kw-hr, 4 ft³ lb/sq in., 20 liter atmospheres, 25 IT calories, 0.001285 Btu, 1 standard refrigerating ton-hour?

3. State the definition of an absolute kilowatt in terms of dynes and centimeters and derive the factor for converting from kilowatt-hours to foot-pounds.

4. Invent a thermometer, preferably a type you have never heard of, and define a temperature scale in terms of it.

5. Using the terms work and heat in the thermodynamic sense write $Q+$ for heat to the system, $W+$ for work done by the system, and $Q-$ and $W-$ respectively for heat from and work on the system, in the following cases. If there is no heat write $Q = 0$; if there is no work write $W = 0$. The italicized words in the first sentence in each example define the system.

(a) *The air in a tire and connected tire pump.* The pump plunger is pushed down, forcing air into the tire. Assume tire, pump walls, and connecting tube non-conducting.

(b) *The water and water vapor in a rigid metallic container.* The container is set on a stove, and the pressure and temperature of its contents rise.

(c) The system in (b) bursts its container and explodes into a cold atmosphere.

(d) *Liquid in a non-conducting vessel.* The liquid comes to rest from an initial state of turbulent motion.

(e) *Hydrogen and oxygen in a combustible mixture within a non-conducting and rigid envelope.* A spark which may be considered infinitesimal and negligible causes the two gases to combine.

(f) *Hydrogen and oxygen in a combustible mixture forming a bubble in a large reservoir of water.* A minute spark, as in (e), causes them to combine.

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CHAPTER II

THE FIRST LAW OF THERMODYNAMICS

Introduction to the First Law

Consider a system (Fig. 1) consisting of a fixed surface S and a weight ω tied to a drum mounted above the surface in frictionless bearings. Let us call the state of this system in which the weight rests upon the surface state 1.

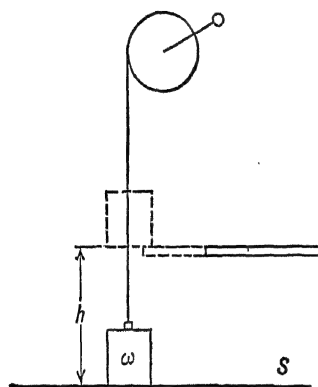


FIG. 1

A process occurs in which some outside agent turns the crank on the drum and causes the weight to move slowly upward until it is elevated a distance h above the surface. This new state of the system we shall refer to as state 2. The process just described was accompanied by a flow of work from a system comprising the agent and to the system comprising the weight and drum, in accordance with the definition of work:

Work flows from a system (and to another) during a given operation if the sole effect external to the system could be the rise of a weight.

Next, the weight-drum system is allowed to return to state 1 by a slow downward movement of the weight. In order to insure slow motion it is necessary to apply a restraining force to the drum. It is apparent that the restraining force might be the force applied by an opposing weight, of the same magnitude as weight ω but outside the system, which will rise the distance h as the system returns to state 1.

Following the convention that *work done by the system is positive* and work done on the system is negative, we may write for the cycle of operations 1-2-1

$$\oint dW = 0,$$

where the circle on the sign of integration indicates that the summation is made around a closed cycle.

It appears that something which was supplied to the system as work in process 1-2 was not destroyed or even diminished in the course of

the operations, because an equal amount of work was returned to the surroundings by the system when the original state was restored. It is not proper in view of our definition of work to say that the work was stored in the system at state 2, but we recall that in the science of mechanics the stored something is referred to as potential energy due to gravity.

Now let us repeat process 1-2 exactly, but, instead of opposing process 2-1 with an external weight, let us restrain the downward motion by means of a brake on the drum. When the weight is once more resting on the surface we inspect the system to see if state 1 has been restored. We find that it has been restored in every respect except one; namely, the temperatures of the drum and brake shoe are higher than in state 1.

Our experience with heat indicates that even in this respect we may return to state 1 by cooling the brake and drum. Now for this second cycle of operations we may write

$$\oint dW \neq 0,$$

and our concept of a something which is conserved to appear as work or to be stored as potential energy fails.

Let us speculate as to the possibility of inventing a new manifestation or phase of this something which will account for its seeming disappearance during the operation of the brake. We might assume, for instance, that the new phase is heat, an assumption which might be defended for a time if we can show that there is a functional relationship between the quantity of work unaccounted for and the quantity of heat present in a cyclic process. This assumption might be verified by lifting various weights through a certain change in level and measuring the quantity of heat delivered to a calorimeter by the system as it returns to its original state (Fig. 2).

Experiments of this sort have been carried out, and they show that the work done in raising the weight is proportional to the heat delivered by the system to the calorimeter. Therefore we may write

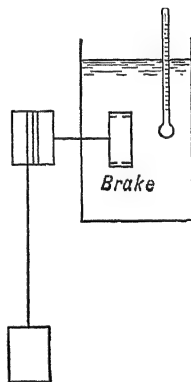


FIG. 2

$$J \oint dQ - \oint dW = 0 \quad [1]$$

where $\oint dW$ denotes the algebraic summation of the quantities of work,

positive or negative, $\oint dQ$ the algebraic summation of the quantities of heat, and J a factor of proportionality.

The First Law of Thermodynamics

The first law of thermodynamics is simply a generalization of [1] to include all cyclic processes in nature: *If any system is carried through a cycle (the end state being precisely the same as the initial state) then the summation of the work delivered to the surroundings is proportional to the summation of the heat taken from the surroundings.* The summations are in both instances algebraic and include positive and negative heat and work.

It should be noted that the experiments cited above are by no means a proof of the First Law. They do not include an example of that large class of cases in which a net amount of work is delivered to the surroundings (or $\oint dW > 0$). Furthermore, any statement as general as this one, unless it rests upon some principle which is still more general, cannot be proved. If it is true it is probable that its truth will never be demonstrated except by the failure of all attempts to disprove it.

The Proportionality Factor, J

By means of any cycle executed by any system we may find the proportionality factor J of [1] corresponding to prescribed units of work and heat. For example, two units of heat that were commonly employed before and after the enunciation of the First Law are the 15-degree *calorie* and the 60-degree *British thermal unit*. A quantity of heat expressed in 15-degree calories is the number of grams of water that will be raised by it from 14.5 to 15.5 degrees Centigrade while under a pressure of 1 standard atmosphere. A quantity of heat expressed in 60-degree British thermal units is the number of pounds of water that will be raised by it from 59.5 to 60.5 degrees Fahrenheit while under a pressure of 1 standard atmosphere. Experiments have shown, through [1], that J corresponding to the 15-degree calorie and the kilogram-meter is 0.427, and that J corresponding to the 60-degree British thermal unit and the foot-pound is 778.

The value of J is as arbitrary as the choice of units for either Q or W . For example, if we choose the kilogram-meter as the unit of work, it is always possible to devise a heat unit of such magnitude that J is unity. For we may vary the unit of mass or the prescribed temperature interval or the fluid specified in the definition of the heat unit. When J is unity the units of heat and work are called by the same names. Thus we have the kilogram-meter of heat or the foot-pound of heat. Conversely, we

have the 15-degree calorie of work, the 60-degree British thermal unit of work, etc.

In this fashion the First Law eliminates the need for a dual system of units for work and heat. We may, if we please, discard all the old heat units defined in terms of prescribed fluid, unit of mass, and temperature interval and retain only the usual work units. Such a step would remove the necessity for changing the value of J each time a presumably more precise measurement of work and heat is made. It would also simplify scientific literature by reducing the number of units which may be employed. However, custom and the convenience of a unit which corresponds to unit rise in temperature of unit mass of water have hitherto prevented this simplification.

Heat units may still be abandoned without offending custom or convenience by defining a calorie of work and a British thermal unit of work each of such magnitude as to give proportionality factors close to unity when paired respectively with the old calorie of heat and the old British thermal unit of heat. Such a definition, in terms of electrical work units, was proposed by the First International Steam Tables Conference at London in 1929.* It is as follows: 1 international steam-table calorie (1 IT cal) = $1/860$ international watt-hours. The conversion from this calorie to kilogram-meters is found from this definition to be given by the equation

$$1 \text{ IT cal} = 0.42699 \text{ kg-m.}$$

The conversion factor differs from the J corresponding to 15-degree calories and kilogram-meters by less than the experimental uncertainty in the value of J .

The British thermal unit corresponding to the IT calorie is defined through an equivalence between compound units, which was approximately true for the old heat units — namely,

$$1 \text{ Btu/deg F lb} = 1 \text{ IT cal/deg C g.}$$

From this and the definition of the IT calorie the conversion from British thermal units to foot-pounds is found to be given by the equation

$$1 \text{ Btu} = 778.26 \text{ ft-lb.}$$

Through subsequent pages the term calorie will be used to denote the IT calorie and the term Btu to denote the corresponding British thermal unit. Also we shall assume in all equations that the units are consistent — that is, the value of J is unity and the units of work and heat have

* *Mechanical Engineering*, Vol. 52 (1930), p. 120.

the same name. Thus [1] becomes

$$\oint dQ - \oint dW = 0. \quad [1a]$$

Corollaries of the First Law

The Definition of Internal Energy, a Property. Consider a system which can change by some process *A* from state 1 to state 0 (Fig. 3), and by some process *B* from state 0 to state 1. Then, by the First Law [1a], we may write

$$\int_{1A}^0 (dQ - dW) + \int_{0B}^1 (dQ - dW) = 0.$$

Let process *C* be any other process by which the system may change in state from 0 to 1. Then for the cycle 1AOC1 we may likewise write

$$\int_{1A}^0 (dQ - dW) + \int_{0C}^1 (dQ - dW) = 0.$$

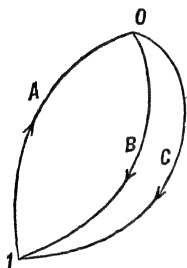


FIG. 3

Combining these two equations and simplifying, we get

$$\int_{0B}^1 (dQ - dW) = \int_{0C}^1 (dQ - dW).$$

Therefore, when a system changes from one prescribed state to another, the value of the integral of $(dQ - dW)$ is fixed by the end states and is independent of the process. It follows that this integral is a property because it satisfies the criterion of a property as stated on page 7. We shall call it the *internal energy* of the system and give it the symbol *E*: thus,

$$E_1 - E_0 = \int_0^1 (dQ - dW) = Q - W, \quad [2a]$$

where *Q* and *W* denote respectively the net heat received by the system and the net work done by the system during the change of state from 0 to 1. Differentiation of [2a] gives the expression

$$dE = dQ - dW$$

or

$$dQ = dE + dW. \quad [2]$$

Thermodynamics tells us nothing about the values of E_1 or E_0 in [2a], though it does tell us, through [2a], the means of computing the difference between them. Since there is no absolute value of the internal energy, it is permissible to assume its value to be zero at any specified state. Then if measurements are made of the heat and work

involved in passing from that state to a second state the corresponding value of the internal energy in the second state may be found through [2a]. Obviously, the difference between such values for any pair of states may be substituted for the left-hand member when [2a] is applied to a process joining that pair of states.

It is profitable to dwell on the distinction between the property E on the one hand and the non-properties Q and W on the other. In the section called Introduction to the First Law it was pointed out that the cyclic integral of dQ or of dW may be other than zero, which is proof enough that the integrals of these quantities are not properties. On the other hand [1a] and [2] in combination show that the cyclic integral of dE cannot be other than zero.

The differential dE is an exact differential in terms of the variables (the independent properties) that determine the state. That is, the value of its integral is fixed, except for an arbitrary constant, when the values of the independent variables are fixed. No similar statement can be made concerning the differentials dQ and dW , because the values of their integrals depend on the processes by which the state is approached and not upon the magnitudes of the properties corresponding to the state. Thus, we may use the symbol E_1 to denote the internal energy corresponding to a state 1; but the corresponding symbols W_1 and Q_1 would not be employed, because there is no quantity of work which corresponds to state 1 (no matter how the reference state may be selected), nor is there a quantity of heat corresponding to state 1.

The Law of Conservation of Energy. The Law of Conservation of Energy may be stated as follows: *The internal energy of a system remains unchanged if the system is isolated from its environment as regards work and heat, regardless of the nature of the changes within the system.** If one part of the system should suffer a decrease in internal energy, the remaining parts would experience an increase of precisely the same magnitude. Moreover, *the internal energy, being a property, remains unchanged for any cyclic change in the state of the system.* It is easy to show that the above statement of the Law of Conservation of Energy is entirely equivalent to the First Law in the form [1].

The Definition of Energy. The term energy may be employed as a general term which embraces heat, work, and internal energy. Each of these has been defined previously.

In terms of our experience in other sciences we find internal energy to be inclusive. For example, into a system comprising a marble in a

* Therefore, it is sometimes said, after Clausius, "the energy of the universe is constant." This is a bold — and unnecessary — extension of a principle which relates to finite systems.

bowl, work may be introduced to give the marble a finite velocity. The corresponding increase in the internal energy of the system is called in mechanics the increase in *kinetic energy*. Again, into a system comprising a weight in a gravitational field, work may be introduced to raise the weight. The corresponding increase in the internal energy of the system is called in mechanics the increase in *potential energy due to gravity*. Similarly, internal energy may include potential energy in an electrostatic field or in a magnetic field. These are all forms of stored energy which may be increased or decreased through the transfer of work alone. Internal energy includes besides these all the kinds of stored energy which are affected by transfer of heat.

The First Law and the Boundaries of a System

The First Law states that work and heat are equal in a cyclic process. The quantities of work and heat, as explained in Chapter I, are evaluated at the boundaries of a system. If the system consists of a block of copper which is exposed to an external block of different temperature, then heat will flow. But if both blocks are within the boundaries of the system the same effects will involve no heat. Similarly, if the system consists of a weight which is raised to a higher level by the fall of an external weight, then work flows. But if both weights are within the boundaries of the system the same effects will involve no work.

From these considerations it may be seen that no application of the First Law can be made until the system and its boundaries are defined. The boundaries need not be stationary, and in general they will not be. They may extend or contract in accordance with the behavior of the matter which constitutes the system, but they must always enclose the same collection of matter. In any event, *the first step in the solution of a problem in thermodynamics is the description of a system and its boundaries.*

PROBLEMS

1. Explain why work and heat are not properties of a system, using the weight-pulley-brake system of Figs. 1 and 2 as an example.

2. A system executes a cyclic process during which there are four heat transfers; namely,

$$Q_1 = 224 \text{ cal}, \quad Q_2 = -20 \text{ cal}, \quad Q_3 = -200 \text{ cal}, \quad Q_4 = 37 \text{ cal}.$$

At four points work is done, three of which are $W_1 = 50 \text{ watt-sec}$, $W_2 = -40 \text{ watt-sec}$, $W_3 = 75 \text{ watt-sec}$. What is the fourth work quantity, and is it done on or by the system?

3. A system executes a process during which

$$Q = 224 \text{ IT cal and } W = 50 \text{ watt-sec (international joules)}.$$

How much does its internal energy increase (increase +, decrease -)?

4. A system executes a process between a temperature of 100 degrees and a temperature of 200 degrees. The heat transferred per degree increase in temperature at each temperature attained during the process is given by the equation

$$\frac{dQ}{dt} = 0.5 \text{ Btu/degree.}$$

The work done *by* the system per degree increase in temperature at each temperature attained is given by the equation

$$\frac{dW}{dt} = 1 - 0.01t \text{ Btu/degree.}$$

Find the increase in internal energy of the system during the process:

5. The internal energy of a certain system is a function of temperature only and is given by the expression

$$E = 25 + 0.25t \text{ IT cal.}$$

When this system executes a certain process the work done by it per degree temperature increase is

$$\frac{dW}{dt} = 0.1068 \text{ kg-m/degree.}$$

Find the heat transferred when the temperature changes from 100 degrees to 200

6. A revolving flywheel having a kinetic energy of 1,000,000 ft-lb is brought to a dead stop by a piston as the piston compresses air in a cylinder. Neglect all friction between piston and cylinder and in flywheel bearings, and assume the piston and cylinder walls non-conducting. How much has the internal energy of each of the following systems increased?

- (a) The air within the cylinder.
- (b) The flywheel-piston combination.
- (c) The whole mechanism.

Consider the systems described as surrounded by non-conducting envelopes which constitute the boundaries of the system, and neglect the work done against the atmosphere.

7. A fanwheel in a room having non-conducting walls is allowed to coast to a full stop, no power being delivered to it. Considering the system bounded by the walls of the room,

- (a) Is the work $+$, $-$, or 0? ✓
- (b) Is the heat $+$, $-$, or 0? ✓
- (c) Is the increase in internal energy $+$, $-$, or 0?

8. State whether the internal energy increases, remains the same, or decreases for the system of each process described in problem 5 of Chapter I.

SYMBOLS

- E internal energy of system in general
- J proportionality factor

Q	heat to system
W	work from system
\oint	summation made around a closed cycle

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CHAPTER III

THE PURE SUBSTANCE

Independent Properties and Dependent Properties

In some systems it is necessary to prescribe a large number of independent characteristics or properties before the state is defined. Even in the simple system described on page 8 which consists of the weight, cord, drum, brake, and surface it is necessary to define the state not alone in terms of the position of the weight, but also in terms of the temperature of the brake and the temperature of the drum. If the weight is allowed to fall unrestrained to the surface the temperature of the weight and the temperature of the surface must be included as important and independently varying properties.

It should be remembered that all observable or measurable characteristics are properties, but all need not be independent properties. For example, the diameter of the brake drum increases slightly when it is used to restrain the falling weight, but it can be shown that for each temperature of the brake drum there is a corresponding diameter. Therefore, measurement either of the diameter of the drum or of its temperature may be used to identify the state; measurement of both is unnecessary. If temperature is considered an independent variable, then drum diameter is a dependent variable, and conversely.

Let P denote a dependent property and $x_1, x_2, \dots x_n$ enough independent properties to determine the state of a system. When the quantities $x_1, x_2, \dots x_n$ are fixed, then the quantity P is fixed. The mathematical statement of this fact is as follows:

$$P = f(x_1, x_2, \dots x_n),$$

where f denotes a function. This equation may be interpreted geometrically by the following statement: *There is a continuum in $n + 1$ dimensions which represents the relationship between $P, x_1, x_2, \dots x_n$ — a dimension being assigned to each of these quantities.* If there are two independent properties, as for pure gases and liquids, then there is a surface in three-dimensional space which will represent the relation between two independent properties and a dependent one.

Any change in the property P may be expressed in terms of its partial derivatives and the changes in the independent properties; thus

$$dP = \frac{\partial P}{\partial x_1} dx_1 + \frac{\partial P}{\partial x_2} dx_2 + \cdots \frac{\partial P}{\partial x_n} dx_n.$$

As an example of the application of this equation consider a system having two independent properties, x_1 and x_2 . Then the differential of the dependent property P is given by the equation

$$dP = \frac{\partial P}{\partial x_1} dx_1 + \frac{\partial P}{\partial x_2} dx_2.$$

The partial-differential calculus teaches that, if P is a function of x_1 and x_2 , then the magnitude of the second derivative of P with respect to x_1 and x_2 is independent of the order of differentiation: thus

$$\frac{\partial}{\partial x_2} \left(\frac{\partial P}{\partial x_1} \right) = \frac{\partial}{\partial x_1} \left(\frac{\partial P}{\partial x_2} \right).$$

If, then, we have an expression of the form

$$dP = M dx_1 + N dx_2,$$

it follows that

$$\frac{\partial M}{\partial x_2} = \frac{\partial N}{\partial x_1},$$

*provided that P is a property of the system.** This is another test by which a property may be identified.

The Pure Substance

A system which is homogeneous in composition and homogeneous and invariable in chemical aggregation is called a *pure substance*. For example, a system consisting of pure oxygen existing as a vapor, a liquid, a solid, or any combination of these is a pure substance. The same may be said as regards ordinary water. Air may be considered a pure substance as long as it is all vapor or all liquid. However, if part is liquid and part vapor, then it is no longer a pure substance, for the liquid will be richer in nitrogen than the vapor. Again, a mixture of one mole of hydrogen gas and one-half mole of oxygen gas is a pure substance as long as no liquid or solid phase appears. On the other hand, if in one part of the system the constituents are combined chemically in the form H_2O , the system is not a pure substance, because though homogeneous in composition it is not homogeneous in chemical aggregation. Moreover, if the entire system changes in the course of a

* In the language of mathematics, dP is an exact differential if $\partial M / \partial x_2 = \partial N / \partial x_1$.

process to the form H_2O , it would not be considered a pure substance during that process because it is not invariable in chemical aggregation.

It is known from experience that *a pure substance in the absence of motion, gravity, capillarity, electricity, and magnetism has only two independent properties.** Among the familiar properties of a pure substance which can be quantitatively evaluated are pressure, temperature, specific volume, internal energy, viscosity, and electrical resistivity. As our experience in thermodynamics and in other sciences is broadened we can add to this list. From among these we may select two, and if these two prove to be independent of each other, then when their values are fixed the values of all the others are fixed. If after a change of state the initial values of our two selected properties are restored, then the initial values of all the other properties will be restored. Commonly any two properties will be independent of each other, though there are obvious exceptions: for example, a property cannot be independent of another in terms of which it is defined, thus, the specific volume cannot be independent of the density, nor the electrical resistivity of the electrical conductivity. A less obvious exception is the combination of pressure and temperature — these properties are independent of each other for a pure substance in the vapor phase or in the liquid phase, but not for a mixture of phases.

The Symbols e , u , E , and U

A system consisting of a pure substance in a homogeneous and stable state has two independent properties in the absence of motion, gravity, electricity, magnetism, and capillarity. Therefore, we may state that the internal energy of a 1-pound mass of such a system is a function, for example, of temperature and volume of the unit mass. To this function we shall give the symbol u , whereas the symbol e may be used to denote the internal energy of a unit system in general. Thus, for the conditions specified, we may write

$$e = u(t, v), \quad \text{or simply } e = u.$$

Values of the function u may be arranged in a table according to values of two arguments, such as temperature and volume or temperature and pressure. Values of e could not be arranged in such a simple table, because e changes not only with changes in temperature and

* This statement is strictly true only for liquid and gaseous states. Under the conditions specified a solid may have different pressures in different directions (for example, tension in one direction and compression in another). Thus, for a single independent property — the pressure — would be substituted several independent properties. Two properties will suffice to determine the state only if pressure is the same in all directions.

volume, but also with changes in motion, height, electrostatic charge, position in an electrostatic field, etc. Therefore, we distinguish between u , the function of two variables, and e , the function of many variables. Following the usual convention we shall use the capital letters U and E to denote the corresponding quantities for systems that are not of unit mass. Thus,

$$U = \int u \, dm \quad \text{and} \quad E = \int e \, dm,$$

where integration is taken over all elementary masses that constitute the system.

State Changes in a System Consisting of a Pure Fluid Substance

The Constant-Volume Process (the Isometric). Consider a system consisting of a unit mass of a pure fluid substance uninfluenced by gravity, electricity, capillarity, or magnetism. If this system is confined within a chamber of invariable volume a change in the state of the fluid can be accomplished by either: (a) rotating a paddle wheel within the fluid, by means of an external falling weight, for instance; or (b) adding heat by the application of a body at higher temperature (S , Fig. 4).

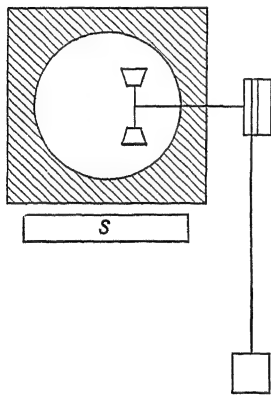


FIG. 4

Let us perform two experiments, one of the heating type and one of the paddle-wheel type, each starting from the same state (the same pressure, temperature, specific volume, total volume, internal energy, etc.). In the heating experiment no work is done by or on the system. Therefore, we may write, by [2],

$$dQ = du.$$

In the paddle-wheel experiment no heat need flow, but the paddles apply a force to the fluid and move it through a distance. This operation constitutes the application of work to the fluid and results in acceleration and motion of parts of the system. The motion will vanish after the completion of the operation. We may write for the paddle-wheel experiment, by [2],

$$0 = du + dW.$$

Now, if the heat added in one experiment is made numerically equal to the work added in the other (the same number of calories or the same number of foot-pounds), the final internal energy will be the same

for both experiments. Moreover, since the specific volume remains unchanged in both experiments, the final specific volumes will be identical. The equivalence of the two independent properties, specific volume and internal energy, is sufficient to insure equivalence of the two final states.

Here we have two processes with the same initial states and the same final states. The changes in all properties are the same in both, and the identity of these changes makes evident the identity of the end states. On the other hand the work involved is less than zero in one process and zero in the other. The heat is zero in one and greater than zero in the other. If the heat and work in these processes had represented properties or changes in properties, their values would have been the same in both instances. They are different because *the end states of a process do not fix the values of heat and work*.

The ratio of the increase of internal energy in a constant-volume process to the corresponding increase in temperature expressed as a derivative, is called the *specific heat at constant volume*. Thus

$$c_v = \left(\frac{\partial u}{\partial t} \right)_v$$

Evidently the term specific heat is a misnomer unless its definition includes a sufficiently circumscribed description of the process in which at constant volume $du = dQ$. Nevertheless we shall use this term because it is so generally accepted; but it must be understood that it represents the rate of change of a property with temperature rather than a quantity of heat.

The Constant-Pressure Process (the Isopiestic). If a fluid is confined in a cylindrical chamber closed at the top by a weighted piston which can move up and down frictionlessly and without clearance (Fig. 5), its pressure will remain constant for any process which is carried out slowly. As in the constant-volume process, work or heat can be added to the fluid under the piston. In either event the volume occupied by the fluid will change and the piston will move to a new position. Let us consider a system consisting of unit mass of fluid. The work done by this system on its surroundings is the product of a force and the distance through which it moves; thus, for a slight outward motion of the piston the work done on the piston is $pa \, ds$ or $p \, dv$, where a denotes the area of the piston, ds the distance the piston moves, and dv the increase

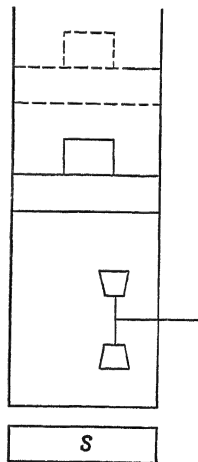


FIG. 5

in the volume occupied by the system. Equation [2] applied to the heating process becomes

$$dQ = du + p dv;$$

applied to the paddle-wheel process it becomes

$$0 = du + p dv - dW_p,$$

where dW_p denotes a positive number representing the amount of work done by the paddle wheel *on* the system.

Since p is constant we may write for $(du + p dv)$ the single differential $d(u + pv)$, in which v denotes the specific volume of the fluid. Now the quantity $(u + pv)$ is made up entirely of properties, that is, it is made up of quantities whose change is fixed by the end states. Therefore it is itself a property, because the change in it is fixed by the end states and is independent of the process by which the change occurs. Its usefulness in several types of problems justifies assigning to it a name and a symbol. It is called *enthalpy* (pronounced en-thal'-py), and the symbol for its value per unit mass of substance is h .

The paddle-wheel work in the first constant-pressure process is consequently given by

$$dW_p = dh,$$

and the heat in the second by

$$dQ = dh.$$

If the initial states are the same in both processes and the heat in the second is equal to the paddle-wheel work in the first, then the final enthalpies and pressures will be respectively the same for the two and the final states will be identical.

The ratio of the increase in enthalpy in a constant-pressure process to the corresponding increase in temperature, expressed as a derivative, is called the *specific heat at constant pressure*. Thus

$$c_p = \left(\frac{\partial h}{\partial t} \right)_p$$

As in its constant-volume counterpart, the term specific heat is a misnomer, but we shall use it with the understanding that it represents the rate of change of a property with temperature rather than a quantity of heat.

Representation of Changes of State on Diagrams. Any change of state which consists of a continuous series of homogeneous states assumed by a pure substance can be represented on a diagram having any pair of independent properties as coordinates. In Fig. 6 a constant-volume

change and a constant-pressure change are shown respectively by lines OV and OP on the pressure-volume plane, the temperature-pressure plane, and on the plane of internal energy and volume.

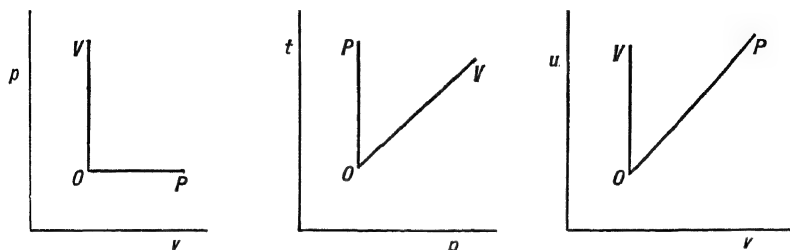


FIG. 6

Homogeneity is never realized in any finite process which is completed in finite time — for instance, the fluid at the bottom of the constant-volume chamber is warmer than the fluid above it if heat is supplied at a finite rate. Nevertheless, many actual processes are carried out slowly enough to avoid serious departure from homogeneity, and these may be adequately represented on a diagram of properties.

The Process at Constant Internal Energy. For any change of state at constant internal energy [2] becomes

$$dQ = dW;$$

that is, the heat supplied to a system from its surroundings must be exactly counterbalanced by the work done by the system on its surroundings, or else there must be neither heat nor work. A process based on the second of these alternatives can be executed as follows:

A system consisting of a unit mass of fluid is confined in one part of a chamber, the walls of which are perfectly non-conducting to heat,

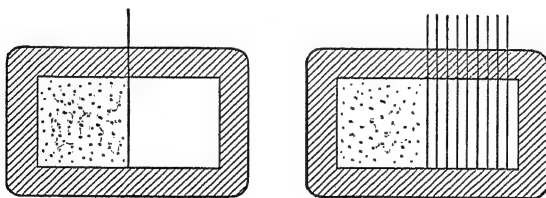


FIG. 7

by a thin partition. The remaining space within the chamber is exhausted of all matter (Fig. 7). When the partition is removed through a slot in the wall of the chamber the fluid flows rapidly into the space

beyond, while its volume increases and its pressure decreases. The temperature will probably decrease.

As this process does not consist of a succession of homogeneous states, it cannot be represented by a line on any diagram of properties. But any number of intermediate homogeneous states can be obtained by providing a large number of thin partitions in the exhausted space which can be withdrawn successively beginning with the one restraining the fluid. If the number of partitions is increased indefinitely the various states of the system trace out a line of constant internal energy on a diagram of properties.

Another process at constant internal energy can be devised in accordance with the first alternative discussed above. The fluid is confined in a cylinder behind a piston which is held in place by a force (Fig. 8). The force is reduced just enough to allow the piston to move slowly outward, while a hot body is applied to the end of the cylinder in such manner as to cause a flow of heat exactly equal to the rate at

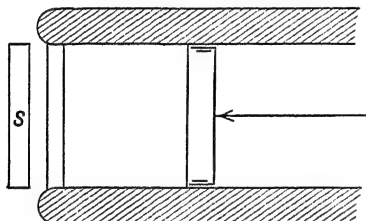


FIG. 8

which the system does work on the piston. Of course, the control of this process presents grave difficulties in contrast to the case with which the experiment of the partitioned chamber can be carried out. Despite the differences in mechanism, in difficulty of execution, and in quantities of work and heat involved, these two

processes at constant internal energy can be represented by the same line on a diagram of properties, provided that they have the initial state in common.

They differ in one respect that will be of importance in later discussions: namely, the piston process can be reversed so that the system retraces the path which it followed in the original experiment as it receives work and rejects heat exactly equal in magnitude respectively to the work done and the heat received originally. The system in the partition experiment cannot be made to retrace its path without introducing quantities of work and heat which played no part in the original process.

The Constant-Temperature Process (Isothermal). Both the processes at constant internal energy which are described above can be converted to constant-temperature processes if the fluid is made to communicate through conducting walls with a constant-temperature bath. Under these circumstances it is probable that heat will be transferred in the partition process as well as in the piston process. For the partition

process [2] becomes

$$dQ = du,$$

whereas for the piston process it is

$$dQ = du + dW.$$

Since the change in u is the same for two processes joining the same two states the heat transferred in the piston process will exceed the heat of the partition process by the work done by the system on the piston.

Work Done on a Piston. If a fluid is confined within a cylinder by a piston, work will be done by the fluid if the piston is allowed to move outward — that is, toward larger volumes of the fluid. If the motion is slow enough we may assume that the pressure exerted by the fluid on the piston will be the same as the pressure exerted on the cylinder walls. (This assumption is satisfactory even for the highest speeds attained by pistons in reciprocating engines.) For any small expansion in which a unit mass of fluid increases in volume by an amount dv the work done by the fluid on the piston is given by

$$pa \, ds = p \, dv,$$

where a denotes the area of the piston and ds the distance through which the piston moves. Therefore, the total work done on a piston during any process is the integral of $p \, dv$ or the area under the curve representing the process on a p - v diagram.

However, work and the integral of $p \, dv$ are not always equal or equivalent, and great care must be exercised in making the substitution. It should be noted that, of the two experiments described above which employ multiple partitions (that at constant energy and that at constant temperature), both have finite values of the integral of $p \, dv$ and zero values of work. In the paddle-wheel experiment at constant volume the integral of $p \, dv$ is zero and the work done by the system is less than zero. *The substitution of $p \, dv$ for dW can be made only if all the work involved in the process is done by the fluid on a moving boundary on which it exerts at all times the same pressure that it exerts on its stationary boundaries.* Sometimes, as in the paddle-wheel experiment at constant pressure, dW can be separated into two parts, one of which is $p \, dv$ and the other a work which must be determined otherwise.

Adiabatic Processes. A process which involves no heat is called an *adiabatic process*. The process at constant internal energy in which the partition is withdrawn is an adiabatic process. On the other hand, the expansion at constant internal energy involving work on a piston and heat is not an adiabatic process. The same path may correspond to an

adiabatic process if followed in one fashion and to a non-adiabatic process if followed in another.

One simple adiabatic process consists of a slow expansion (or compression) of a fluid behind a piston, the piston and cylinder walls being perfect heat insulators. For this process [2] becomes

$$0 = du + dW.$$

Here we may substitute $p dv$ for dW and obtain

$$du = -p dv.$$

The path of this type of expansion can be traced on a diagram of properties of the fluid provided that the relation between p , v , and u is known for the fluid in the cylinder — that is, internal energies must be available in the form of charts, tables, or algebraic equations, for all combinations of pressure and specific volume.

The equation given above may be written

$$\frac{du}{dv} = -p.$$

Thus, if the initial state is represented by the point P in the u - v diagram of Fig. 9, the initial slope on the diagram may be laid off equal to minus the initial pressure. The curve may

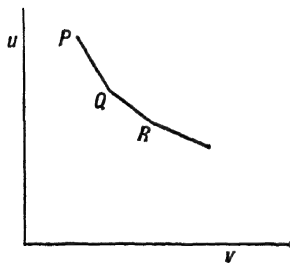


FIG. 9

be approximated by following this slope for a short distance to Q where the corresponding pressure may be determined from u , v , and the known relation, and a new slope may be laid off. A second step may be made to R , and so on until enough of the curve has been located. Several methods of finite-step integration have been devised for the solution of this type of problem. The crude one just outlined serves adequately to illustrate the method. Once the u - v curve has been drawn the path of the process can be traced on any other diagram such as a u - p or a p - v diagram.

If the relation between u , p , and v is available in algebraic form then it is quite possible that a complete algebraic statement can be found for the relation between any two properties, such as p and v , for this type of adiabatic expansion. For instance, the u - p - v relation for some gases may be represented satisfactorily over a wide range of conditions by an equation of the form

$$u = A + Bpv.$$

where A and B are constants. Then for any process we get

$$\frac{du}{dv} = B \left(p + v \frac{dp}{dv} \right)$$

by simple differentiation; and, since for adiabatic expansion behind a piston $du/dv = -p$, we may write

$$B \left(p + v \frac{dp}{dv} \right) = -p,$$

or

$$\frac{B}{1+B} \frac{p}{v} \frac{dv}{dp} = -\frac{d \ln v}{d \ln p}.$$

Integrating we get

$$pv^k = \text{constant},$$

where

$$k = \frac{B+1}{B}$$

PROBLEMS

1. One pound of air can be expanded from 100 lb/sq in. abs and 100 F to 50 lb/sq in. abs and 100 F as it does 20,700 ft-lb of work and receives 20,700 ft-lb of heat.

A second kind of expansion can be found between 100 lb/sq in., 100 F, and 50 lb/sq in., 100 F, which requires a heat input of only 10,000 ft-lb of heat.

- What is the increase in internal energy in the first expansion?
- What is the increase in internal energy in the second expansion?
- How much work is done by the air in the second expansion?

2. A system consisting of a pure substance receives 168.7 Btu of heat at constant volume. Next it receives -177.0 Btu of heat as it does -40 Btu of work at constant pressure.

(a) If a process can be found which will restore it to its initial state without a net heat flow to or from the system, how much work will be done by the system during that process?

(b) Fix the value of internal energy in the initial state at zero, and find the corresponding internal energies at the other two states.

3. The specific heat at constant volume of a certain system is constant and equal to 0.25 Btu/F. In a constant-volume process which involves stirring, the temperature of the system increases from 50 F to 150 F while it receives 10 Btu of heat. How much work is done by the system during the constant-volume process?

4. The specific heat at constant pressure of a certain system is a function of temperature only and may be expressed as

$$C_p = 0.5 + \frac{10}{t + 100} \text{ calories/degree C}$$

where t is the temperature of the system in degrees Centigrade.

The system is heated while it is maintained under a pressure of 1 atmosphere until its volume increases from 2000 cm³ to 2400 cm³ and its temperature increases from 0 C to 100 C.

- (a) How much heat is added to the system?
- (b) How much does the internal energy of the system increase?

5(a) On page 50 of the *Steam Tables* by Keenan and Keyes, find the volume, v , and the enthalpy, h , of 1 lb of steam at 100 lb/sq in. abs pressure and at a temperature of 400 F. Find the internal energy of that same 1 lb of steam.

(b) Find a temperature at 128 lb/sq in. abs for which the volume of a pound of steam is the same as at 100 lb/sq in., 400 F.

6(a) How much heat must be transferred to a pound of steam in a constant-volume container to raise its pressure from 100 lb/sq in. to 128 lb/sq in. if its initial temperature is 400 F and no work input occurs?

If the same rise in pressure from the same initial state had been accomplished by stirring, without heat transfer, at constant volume:

- (b) How much stirring work would be done?
- (c) What would be the final internal energy?

7(a) Water at 32 F weighs 62.42 lb/cu ft and ice weighs 57.2 lb/cu ft. Find the work done by a system comprising 1 lb of ice at atmospheric pressure and 32 F as it melts to water at constant temperature and pressure.

(b) If the internal energy of the pound of ice increases by 144 Btu as it melts, how much heat is transferred to the ice during the melting process?

8. The p - v - u relation for a certain gas is given by the equation

$$u = 831 + 0.617 \, pv$$

where u is in Btu per pound, p is in pounds per square inch, and v is in cubic feet per pound. Find the work done by and the heat received by a 1-lb mass of this gas in the following changes in which all work is done on a slowly moving piston:

PROCESS	FROM		TO	
	p	v	p	v
	'sq in.	cu ft/lb	lb/sq in.	cu ft/lb
(a) Constant volume	100	5	150	5
(b) Constant pressure	100	5	100	7
(c) Constant internal energy	100	5	150	

(d) Find the work done in a different kind of process between the same end states as in process (c) if the heat added is 5 Btu/lb.

9. Show that the exponent k in the expression $pv^k = \text{constant}$ is 1.3 for adiabatic expansion behind a piston if the p - v - u relation is given by the equation in problem 8.

10. Express the work done by a gas as it expands behind a piston according to the relation $pv^k = \text{constant}$, in terms of the initial pressure and volume and the ratio of the final pressure to the initial pressure.

11. Compute the work done by a 1-lb fluid system as it expands slowly behind a piston from an initial pressure of 100 lb/sq in. abs and an initial volume of 1 cu ft to a final volume of 3 cu ft in the following expansions:

- (a) Pressure remains constant.
- (b) Pressure \times volume remains constant.
- (c) $pv^{1.3}$ remains constant.
- (d) pv^∞ remains constant.
- (e) The pressure-volume relation tabulated below:

v	p
cu ft/lb	lb/sq in.
1	100
1.5	90.62
2	75
2.5	53.12
3	25

12. If the internal energy decreases by 200 Btu/lb in problem 11(e), how much heat is transferred to the system?

13. A pound of superheated steam contracts slowly behind a piston at a constant pressure of 14.696 lb/sq in. abs from 40 cu ft/lb to 30 cu ft/lb. Find:

- (a) The work done by the steam.
- (b) The increase in internal energy.
- (c) The heat transferred to the steam.

14(a) A pound of steam executes a constant-temperature expansion behind a piston from 1000 lb/sq in. abs to 500 lb/sq in. abs at 700 F. Find the work done by and the heat transferred to the steam during the expansion. (The work must be found graphically from a plot showing intermediate values.)

(b) A pound of steam expands into an exhausted space adjacent to its original container. Initially at 1000 lb/sq in. abs and 700 F it expands to 500 lb/sq in. abs and 700 F. How much heat is transferred to the steam during the expansion?

15. A pound of steam executes a constant-internal-energy expansion behind a piston from 1000 lb/sq in. abs, 700 F, to 800 lb/sq in. abs.

- (a) Find the temperature of the steam when it reaches 800 lb/sq in. abs.
- (b) Find the work done by the steam approximately. (Locate the state at 900 lb/sq in. abs as an aid.)
- (c) Find the heat transferred to the steam.

SYMBOLS

a	area
c_p	specific heat at constant pressure
c_v	specific heat at constant volume
e	internal energy of unit system in general
E	internal energy of system in general
h	enthalpy per unit mass
m	mass
p	pressure
P	dependent property
Q	heat to system
s	distance

u	the quantity U for a system of unit mass
U	internal energy of a system in the absence of motion, gravity, electricity, capillarity, and magnetism
v	specific volume
W	work from system
x_1, x_2	independent properties

SUBSCRIPTS

p	constant pressure
v	constant volume

CHAPTER IV

THE FLOW OF FLUIDS

The Relationship between e and u

It was stated on page 19 that a system consisting of a pure substance in a homogeneous and stable state has two independent properties in the absence of motion, gravity, capillarity, electricity, and magnetism. We use the symbol e to denote the internal energy of unit systems in general and the symbol u to denote the internal energy of a unit system of a pure substance under these restricted conditions. Let us find the relationship between the quantities u and e for a pure substance when neither motion nor gravity is ignored (though we shall continue to ignore capillarity, electricity, and magnetism).

Consider a 1-pound system consisting of a pure substance that is homogeneous in state. Let it be accelerated by a force in such a way that neither its temperature nor its volume is affected. (To accomplish this purpose it is necessary that the force be applied normally to the surface of the fluid system and not through shear.) Then the function u is unchanged in magnitude, though the internal energy e is increased by the amount of work done by the force.

We shall evaluate the change in e in terms of the change in velocity of the system. From the laws of motion we may write

$$F = ma,$$

where F denotes the force applied to the system, m the mass of the system in the physicist's units, and a the acceleration of the system in the direction of the force. During a small interval of time dt the force moves through the distance ds . The work delivered to the system is, therefore, given by

$$F ds = ma ds.$$

The acceleration may be stated as

$$a = \frac{dV}{dt}$$

or as

$$a = \left(\frac{dV}{ds}\right)\left(\frac{ds}{dt}\right) = \frac{V dV}{ds},$$

where V denotes the component of velocity in the direction of the force. Substituting in the expression for $F ds$, we get

$$F ds = mV dV = d\left(\frac{mV^2}{2}\right).$$

Thus, we find that the work done by the force is identical with the increase in the so-called kinetic energy of the system. Upon reaching the velocity V , the system has the internal energy given by

$$e = u + \frac{mV^2}{2},$$

or, since 1 pound mass is $1/g$ units of m (where g is the acceleration given to 1 pound of mass by 1 pound of force),

$$e = u + \frac{V^2}{2g}.$$

If a force F is used to lift our 1-pound system through the change in height dz in a gravitational field of uniform strength, then from the principles of statics we know that

$$F ds = dz,*$$

and the internal energy of the system is increased by the amount dz . Measuring z from an arbitrary datum, we may express the internal energy in terms of the function u , the velocity V , and the height z : thus

$$e = u + \frac{V^2}{2g} + z. \quad [3]$$

The Open System

If a system is so described that matter crosses its boundaries in the course of a change of state, it is called an *open system*.†

Consider a system S , Fig. 10, enclosed within a *fixed boundary* B , and an infinitesimal adjacent mass δm . If the boundary between S and δm is penetrable to δm , the small mass may be made to join the large one inside B . While it is crossing B the surroundings will exert on δm a pressure p .

* Here and in the following pages it is assumed that the acceleration of gravity is identical with g , the acceleration given to unit mass by unit force. If the acceleration of gravity is g' , then the force on unit mass is

$$F = \frac{g'}{g}; \text{ and } F ds = \frac{g'}{g} dz.$$

† This term and the analysis that follows are given by Gillespie and Coe, *J. Chem. Phys.*, **1** (1933), 102-113.

The work done by the surroundings on the compound system comprising S and δm will be, to small quantities of the first order,

$$pv \delta m,^*$$

where v denotes the specific volume of the mass δm as it crosses B . It is assumed, of course, that the boundary B remains fixed in position.

Let us denote the initial and final internal energies of the material within B by E' and E'' respectively, and the initial internal energy of the mass δm by $e \delta m$. Then, for the compound system S and δm , [2] becomes

$$\delta Q = E'' - (E' + e \delta m) - pv \delta m,^\dagger$$

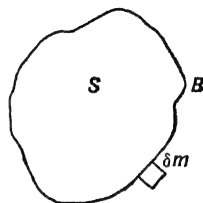


FIG. 10

where δQ denotes heat transferred to S and δm from other things during the process. It was shown in the preceding section that, if motion and gravity are considered, then we may write

$$e = u + \frac{V^2}{2g} + z, \quad [3]$$

so that our equation for the open system becomes

$$\delta Q = E'' - E' - \left(u + pv + \frac{V^2}{2g} + z \right) \delta m.$$

Recalling the definition of enthalpy, h , we may write this

$$\delta Q = E'' - E' - \left(h + \frac{V^2}{2g} + z \right) \delta m, \quad [4]$$

where h denotes the initial enthalpy per unit mass of fluid that crosses the boundary B . Equation [4] may be applied to the transfer of a finite mass across B by summing up values of the first and last terms for all elements of the finite mass. If an element passes outwards across the boundary, then δm is negative and h is its enthalpy per unit mass as it emerges.

* If δm is a cube the force in the direction of its motion is pl^2 , where l denotes the length of a side, and the work is pl^3 . This product is in accord with the statement above. If δm is any other shape, the statement above may be verified by subdividing the shape into elementary cubes.

† Note that the equation $dQ = dE + dW$ holds only for a closed system (such as the compound system described above). It does not hold for an open system — otherwise we could write $\delta Q = E'' - E'$. Moreover, the statement of the First Law

in the form $\oint dQ = \oint dW$ does not hold for an open system.

A simple example to which [4] applies is the adiabatic flow of a gas from a large reservoir or main (the pressure and temperature in which are affected negligibly by the flow) into a small chamber of lower pressure. As the pressure increases in the small chamber the increase in the internal energy enclosed is equal to the initial enthalpy of the fluid that enters.

It is easy to generalize [4] to allow for work crossing the boundary B (by motion of the boundary or otherwise). Let δW_x denote the work passing out through B as the mass δm passes in across B . Then the expression for δQ becomes

$$\delta Q = E'' - E' - \left(h + \frac{V^2}{2g} + z \right) \delta m + \delta W_x, \quad [5]$$

because the total work of the compound system (S and δm) is $(\delta W_x - p v \delta m)$, the latter term in this parenthesis being included in the product $h \delta m$.

Steady Flow

Consider a box B (Fig. 11) which has an opening 1 into which fluid is flowing and another 2 out of which it is flowing. An open system may be described which is bounded by the rigid walls of the box and the imaginary planes 1 and 2 across the corresponding openings. We shall

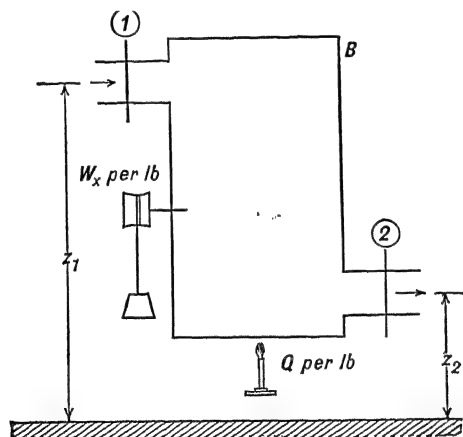


FIG. 11

assume that work is leaving the box by means of a shaft or its equivalent, and that heat is flowing into it, as shown diagrammatically in Fig. 11. To this system [5] may be applied, but the result is more useful if the example is restricted further.

Let us assume the following:

(a) The fluid is uniform in composition, state, and velocity at the entrance, and these things do not change with time.

(b) The same is true at the exit.

(c) The state of the fluid found at any point within the open system is the same at all times.

(d) The mass rate of flow into the open system is constant and equal to the mass rate of flow out of it.

(e) The rates at which heat and work cross the boundary are constant.

An open system for which these assumptions hold is called a *steady-flow system*.

Assumption (c) requires that E'' and E' should be identical, so that [5] simplifies to

$$\sum \delta Q = - \sum \left(h + \frac{V^2}{2g} + z \right) \delta m + \sum \delta W_x. \quad [5a]$$

If these terms are summed up for all the elementary masses crossing the boundary during the period of time required for a unit mass to enter [or, by assumption (d), to leave], [5] becomes

$$Q = \left(h_2 + \frac{V_2^2}{2g} + z_2 \right) - \left(h_1 + \frac{V_1^2}{2g} + z_1 \right) + W_x, \quad [6]$$

where Q and W_x denote respectively the heat passing inward and the work passing outward across boundary B for each unit mass entering the apparatus. *This is the energy equation of steady flow.*

Assumption (c) need not be so rigorous. It is easy to see that, if the states of the fluid at all points within the open system periodically and simultaneously become identical with states previously existing at those points, then [6] holds good. Thus it will apply equally well to a turbine and to a reciprocating steam engine.

The Energy Equation of Steady Flow and Bernoulli's Equation

It was shown on page 32 that if a net force of F pounds is applied to a mass of 1 pound by something other than the gravitational field, and the force is moved through a distance ds in its own direction, then by the laws of motion we may write

$$F ds = d \left(\frac{V^2}{2g} \right) + dz, \quad [7]$$

where V denotes the velocity of the mass and z its height above some horizontal datum plane in the gravitational field of strength g .

Let us consider a stream of fluid in steady flow through a passage. We shall assume that *no shearing stresses exist in the fluid*, so that all

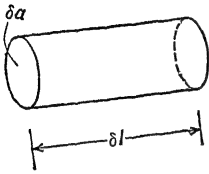


FIG. 12

forces exerted on an elementary mass of fluid by adjacent fluid are normal in direction to the boundary surface of the element. Consider such an element (Fig. 12) whose length δl is in the direction of the resultant velocity V and whose ends are planes of equal area normal to that direction. The

net force applied by adjacent fluid in the direction of V is

$$p \delta a - (p + dp) \delta a = -dp \delta a,$$

where p denotes the pressure on the upstream end, $p + dp$ the pressure on the downstream end, and δa the cross-sectional area of the element. When the element moves through its own length δl , the product of the force and the distance through which it moves becomes $-dp \delta a \delta l$, or $-dp v \delta m$, where v denotes the specific volume of the fluid and δm the mass of the element. We may now apply [7] to the elementary mass of δm pounds, and we get

$$-v dp \delta m = \delta m d \left(\frac{V^2}{2g} \right) + \delta m dz,$$

which may be simplified to the form

$$v dp + d \left(\frac{V^2}{2g} \right) + dz = 0. \quad [8]$$

This is the general form of *Bernoulli's equation* for a steady state of flow.* It is a consequence of the *laws of motion* which were enunciated by Newton 150 years before the enunciation of the First Law of Thermodynamics or the Law of Conservation of Energy.

Despite the anachronism the equation of Bernoulli is often referred to as an energy equation, because it proves to be a restricted form of the First Law. The laws of motion contain within them a principle of conservation for a certain type of hypothetical system. This type of sys-

* For an incompressible fluid [8] may be integrated to the equation

$$pv + \left(\frac{V^2}{2g} \right) + z = \text{constant},$$

which is the form of Bernoulli's equation frequently encountered in hydraulics.

tem has come to be known as a *conservative system*.* No single instance of a conservative system has ever been directly observed in nature, though by deduction we have come to believe that the molecules of a gas constitute such a system. The fluid system that we postulated above is free from shear stresses and is, therefore, a conservative system.

Let us compare the Bernoulli equation [8] with the energy equation of steady flow [6], which we shall reduce to the conditions of the Bernoulli equation by eliminating shaft work, W_x , and by applying the remaining expression to two sections that are separated only by an infinitesimal distance along the stream (Fig. 13). Then we get

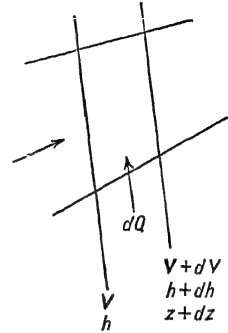


FIG. 13

$$dh + d\left(\frac{V^2}{2g}\right) + dz - dQ = 0, \quad [6a]$$

or, upon expanding dh ,

$$du + p dv - dQ + v dp + d\left(\frac{V^2}{2g}\right) + dz = 0, \dagger$$

as compared with the Bernoulli equation

$$v dp + d\left(\frac{V^2}{2g}\right) + dz = 0.$$

* Maxwell in *Theory of Heat* (Appleton [1885], 92) defines a conservative system in the following terms: "If, in any system of bodies, the force which acts between any two bodies is in the line joining them, and depends only on their distance, and not on the way in which they are moving at the time, then if no other forces act on the system, the sum of the potential and kinetic energy of all the bodies of the system will always remain the same."

† This is an expanded form of the equation

$$de + d(pv) - dQ = 0,$$

as may be seen by comparing it with [3]. This equation may be written

$$v dp + de + p dv - dQ = 0,$$

as compared with the Bernoulli equation, $v dp + d(V^2/2g) + dz = 0$. The two are identical if we may write

$$de + p dv - dQ = d\left(\frac{V^2}{2g}\right) + dz,$$

$$de = dQ - p dv + d\left(\frac{V^2}{2g}\right) + dz.$$

This is true for a fluid system in the absence of electricity, magnetism, capillarity, and fluid shear, for then work received by the fluid results only in compression, acceleration, or change in level.

Since the energy equation of steady flow is true in general, it follows that the Bernoulli equation holds whenever we may write

$$du + p dv - dQ = 0,$$

for then the two are identical. This last equation holds for any process in a pure substance for which u is identical with the internal energy per unit mass and $p dv$ is identical with the net work done by the system. It will be recalled that the property u is a function of only two independent properties, such as pressure and temperature, and is the internal energy in the absence of capillarity, magnetism, and electricity from the standpoint of an observer who sees no variations in velocity or level, that is, an observer who *stands on* the system. The work done by the system would then be $p dv$ in the absence of fluid shear. Therefore it is permissible to write

$$du + p dv - dQ = 0$$

for any fluid system *in the absence of capillarity, electricity, magnetism, and fluid shear*. These are the conditions under which Bernoulli's equation will hold.

The Continuity Equation of Steady Flow

In the solution of steady-flow problems it is often necessary to use in addition to [6] the relationship between velocity, area, and specific volume which is implied in assumption (d) above, which may be stated

$$w = w_1 = w_2,$$

where w denotes the mass rate of flow and subscripts 1 and 2 refer to sections across the path of flow. An equivalent statement is

$$\frac{Va}{v} = \frac{V_1 a_1}{v_1} = \frac{V_2 a_2}{v_2} \quad [9]$$

in which a denotes the area of a cross section of the stream perpendicular to the velocity V . This is the *continuity equation of steady flow*.

Applications of the Energy Equation of Steady Flow

The Joule-Thomson Experiment. The apparatus for the Joule-Thomson experiment consists of a horizontal tube containing a porous plug with pressure gages and thermometers preceding and following the plug. If a fluid is supplied to it at section 1, on one side of the plug, it will flow through, provided that a lower pressure is maintained at section 2 on the other side of the plug (Fig. 14). The energy equation [6] for this example of steady flow becomes

$$h_1 + \frac{V_1^2}{2g} = h_2 + \frac{V_2^2}{2g} + W_x - Q.$$

In the absence of any shaft, or its equivalent, projecting through the wall of the tube, W_x must be zero, and Q may be made to approach zero by applying adequate insulation to the wall. The kinetic-energy terms may be omitted if they are made equal by providing, according to [9], areas in the ratio

$$\frac{a_1}{a_2} = \frac{v_1}{v_2},$$

or by making both V_1^2 and V_2^2 so small that their difference is negligible. Then [6] reduces to the equality

$$h_1 = h_2.$$

Holding always the same initial condition at 1 and reducing the pressure step by step at 2, we could trace by this experiment a line of constant enthalpy on a temperature-pressure diagram. The slope of this line, $(\partial t / \partial p)_h$, is known as the Joule-Thomson coefficient. Generally it is small, but it may be either greater or less than zero. It is positive (decreasing t with decreasing p) for steam and carbon dioxide within the usual range of conditions, and it is negative for hydrogen and for liquid water at room temperature and pressure. The Joule-Thomson experiment is a relatively simple measurement which yields useful information. It has been employed frequently to determine the relations between properties of substances.

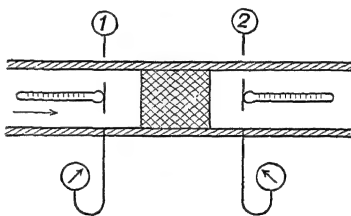


FIG. 14

The Constant-Temperature Expansion. In the apparatus shown in Fig. 14, a heating (or cooling) element could be inserted in the porous plug so that heat might be permitted to flow to (or from) the expanding stream. We learn from the energy equation of steady flow (neglecting change in kinetic energy as before) that the heat transferred from the heating element to the fluid is given by

$$Q = h_2 - h_1.$$

If we should regulate the flow of heat so that the temperatures at 1 and 2 were identical, then, by reducing the pressure step by step at 2 while holding a constant initial state, we could trace the enthalpy-pressure relation along a path of constant temperature. The slope of this path on an enthalpy-pressure chart, $(\partial h / \partial p)_t$, is known as the *constant-temperature coefficient*. Like the Joule-Thomson coefficient it is frequently measured in order to determine the relations between properties of a substance.

Heating and Cooling in Steady Flow. The energy equation of steady flow in the form

$$Q = h_2 - h_1$$

applies to any heating or cooling device, such as a steam boiler or an oil cooler, in which there is no moving mechanism and, therefore, $W_x = 0$, and in which changes in kinetic energy and height between entrance and exit are negligible.

Adiabatic Steady-Flow Processes. As previously stated, an adiabatic process is one in which no heat transfer occurs. The Joule-Thomson expansion is an adiabatic process, but there are others of importance to the engineer. The flow of steam through steam turbines, except those of very small power, may be considered adiabatic, because the heat transfer per pound of steam, Q , through the casing or along the shaft is small as compared with the shaft work, W_x .*

The energy equation of steady flow [6], for any adiabatic case becomes

$$W_x = h_1 - h_2 + \frac{V_1^2 - V_2^2}{2g}$$

if change in elevation may be neglected. This statement is applicable to an entire turbine or to an individual stage of a turbine; it will apply equally well to a centrifugal compressor and its stages.

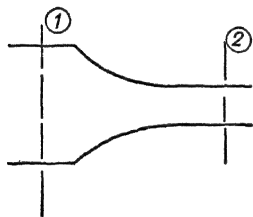


FIG. 15

The flow of steam through a nozzle is another important example of an adiabatic steady-flow process. Imagine a simple converging passage (Fig. 15) through which steam is flowing. The heat transfer per pound of steam, Q , will be small, usually, because a large amount of fluid can be passed through a nozzle of small dimensions.

In the absence of all moving mechanisms W_x must be zero. Therefore [6] becomes

$$\frac{V_2^2 - V_1^2}{2g} = h_1 - h_2$$

If the states 1 and 2 are known, then the increase in kinetic energy in the nozzle can be computed. Conversely, if the increase in kinetic

* For instance a turbine with an uninsulated casing surface of 100 sq ft (not including the exhaust hood which is nearly at room temperature) would give heat to the air of the turbine room at a rate of about 35,000 Btu/hr. Assuming a capacity of 10,000 kw and a steam flow of 100,000 lb/hr to correspond to the 100 sq ft of surface, we find $Q = 0.35$ Btu/lb, which is approximately 1/1000 of the work output, W_x . Of course, insulation would reduce Q to a still smaller fraction of the work.

energy and either state is known, the enthalpy of the other state can be found.

PROBLEMS

1. In a certain Joule-Thomson experiment the low-pressure side is 10 ft vertically below the high-pressure side. The velocity on the low-pressure side is 50 ft/sec, and on the high-pressure side 43 ft/sec. Assuming no heat transfer, compute the change in enthalpy from high side to low side.

2. For the gas of problem 8, in Chapter III, find the ratio of downstream cross-sectional area to upstream cross-sectional area if the pressures in a Joule-Thomson experiment are 75 lb/sq in. abs and 70 lb/sq in. abs, the flow is horizontal, there is no heat transfer, and no change in enthalpy between high side and low side.

3. If the areas in the preceding problem were equal, high side and low side, what would be the change in enthalpy if the initial kinetic energy were 0.1 Btu/lb and the initial specific volume 5 cu ft/lb?

4. A steady flow of steam enters a heating coil at 150 lb/sq in. abs and 400 F and leaves it at 140 lb/sq in. abs and 600 F.

(a) If the kinetic energies at entrance and exit are negligible, how much heat is transferred to each pound of steam as it passes through the coil?

(b) If the coil is 100 ft high and the flow is downward, and the entrance and exit velocities are respectively 200 and 280 ft/sec, how much heat is transferred to each pound between the same end pressures and temperatures?

5. A steam turbine receives a steam flow of 10,000 lb/hr and delivers 500 kw. The heat loss from the casing and the turbine bearing loss are negligible.

(a) Find the change in enthalpy across the turbine if the velocities at entrance and exit and the difference in elevation at entrance and exit are negligible.

(b) Find the change in enthalpy across the turbine if the velocity at entrance is 200 ft/sec, the velocity at exit is 1200 ft/sec, and the inlet pipe is 10 ft above the exhaust.

6. A steady flow of steam enters a condenser with an enthalpy of 1000 Btu/lb and a velocity of 1200 ft/sec. The condensate leaves the condenser with an enthalpy of 70 Btu/lb and a velocity of 20 ft/sec. Find the heat transferred to the cooling fluid of the condenser per pound of steam condensed.

7. The *Steam Tables* give the following values:

	SPECIFIC VOLUME cu ft/lb	ENTHALPY Btu/lb
Saturated steam		
at 100 lb/sq. in. abs	4.432	1187.2
Liquid water		
at 100 lb/sq in. abs and 100 F	0.016	68.2

(a) Compute the amount of heat supplied to each pound of a steady stream of H_2O as it changes in a boiler from water to steam in the respective states given above.

(b) How much does the flow work required to deliver the steam exceed the flow work required to introduce the liquid?

(c) How much does the internal energy of each pound of H_2O increase in the process?

8. A reciprocating engine may be considered a steady-flow device if there is enough "receiver" capacity on either side of it to smooth out variations in pipeline conditions caused by the intermittent action of the engine. The "indicated work" of an engine is the net work done on the piston.

A small reciprocating engine is supplied with steam at 1000 lb/sq in. abs and 760 F. The steam exhausts at 300 lb/sq in. abs and 520 F. If the heat loss from the engine cylinder to the atmosphere is 4000 Btu/hr and the steam flow is 2000 lb/hr, find the indicated power of the engine.

9. In a test of a water-jacketed air compressor it is found that the shaft work required to drive the compressor is 60,000 ft-lb/lb of air delivered, that the enthalpy of the air leaving is 30 Btu/lb greater than that entering, and that the increase in enthalpy of the circulating water is 40.5 Btu/lb of air. From these data, compute the amount of heat passing to the atmosphere from the compressor per pound of air.

10. A nozzle is a device for increasing the velocity of a steadily flowing stream. At the inlet to a certain nozzle the enthalpy of the fluid passing is 1300 Btu/lb and the velocity is 200 ft/sec; at the discharge side the enthalpy of the fluid is 1200 Btu/lb. The nozzle is horizontal, and there is a negligible heat loss from it.

(a) Find the velocity at the nozzle exit.

(b) If the inlet area is 1 sq ft and the specific volume at inlet is 3 cu ft/lb, find the rate of flow.

(c) If the specific volume at the nozzle discharge is 8 cu ft/lb, find the exit area of the nozzle.

11. Steam approaches a horizontal nozzle at a pressure of 100 lb/sq in. abs and a temperature of 500 F through a passage of very large cross section. It reaches the discharge of the nozzle at a pressure of 70 lb/sq in. abs and a temperature of 423 F. Neglect heat loss from the nozzle.

(a) Find the velocity in the nozzle discharge.

(b) Find the area of the nozzle discharge cross section required to pass a flow of 1 lb/sec.

12. Liquid water flows steadily downward through a vertical converging tube. The enthalpy at a point 500 ft above a reference plane is 100.0 Btu/lb; its enthalpy at a point 100 ft above the reference plane is 99.5 Btu/lb. Neglecting heat losses, find the velocity of the water stream at the lower level if its velocity at the upper level is 30 ft/sec.

SYMBOLS

a	acceleration of system in direction of force, area
e	internal energy of unit system in general
E	internal energy of system in general
F	force
g	acceleration given to 1 lb of mass by 1 lb of force
h	enthalpy per unit mass

m	mass in physicist's units
p	pressure
Q	heat to system
ds	small distance
S	system
t	temperature
dt	small interval of time
u	internal energy of unit system in the absence of motion, gravity, electricity, capillarity, and magnetism
v	specific volume
V	velocity, component of velocity
w	mass rate of flow
W_s	shaft work from system
z	height

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CHAPTER V

PROPERTIES OF A PURE SUBSTANCE

A pure substance may in general exist as a solid, a liquid, or a vapor. These different aspects of the substance are known as *phases*. The term phase was introduced into thermodynamics by Willard Gibbs, who used it in a more general sense, namely, *a phase is any physically homogeneous aspect of a system*. Thus a substance may have more than one solid phase, one of which may be amorphous and the others may be different crystalline forms. The boundary between phases is usually sharp and clearly defined, but occasionally, as between vapor and liquid above the critical point, one phase blends into the other and no definite boundary can be detected.

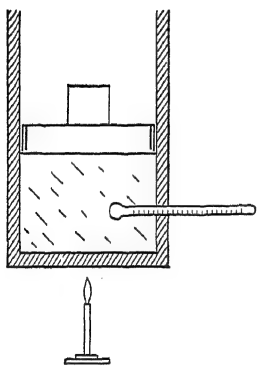


FIG. 16

Let us follow the changes of phase of water under different conditions. Consider a pound of ice at a temperature of 0 F confined in a cylinder by a movable piston which exerts on the ice a pressure of 1 atmosphere (Fig. 16). The temperature of all the ice may be raised uniformly by a slow addition of heat. The heat, as explained on page 22, is equal in magnitude to the increase in enthalpy of the substance; therefore we may use the quanti-

ties of heat as a measure of changes in enthalpy.

When the temperature reaches 32 F the measurements of heat indicate that the enthalpy has increased about 15 Btu. Upon further heating we find at first no change in temperature, despite the increase in enthalpy. During this period the substance exhibits a marked change in appearance when viewed through a glass cylinder. Some of it has become liquid. The proportions of solid and liquid can be changed at will by heating or cooling the substance; but neither heating nor cooling (within certain limits) will cause a change in the temperature. When the enthalpy has been increased by 143 Btu over its value for the solid at 32 F the entire mass will be in the liquid phase and further heating will result in a rise in temperature.

The change in enthalpy between the solid phase and the liquid phase at the same pressure and temperature is called the *latent heat of*

fusion — a choice of words that is unfortunate because the term heat should have been reserved for energy in transit across the boundary of a system by virtue of a temperature difference. Though this change in enthalpy can be caused by means other than heat, such as a revolving paddle wheel in the melted fraction or an electric current passing through the substance, we shall nevertheless adopt the term latent heat because it is commonly accepted.

A latent heat or change in enthalpy at constant pressure and temperature is a characteristic of all well-defined boundaries between phases of a pure substance. In fact it is often used as a means of detecting such boundaries.

Upon further heating, the liquid rises in temperature. At 212 F its enthalpy is found to be 180 Btu higher than that of the liquid at 32 F. Once more we have reached a point where the enthalpy may be increased without change in temperature, and once more we notice a change in the appearance of the substance as the enthalpy is increased. Some of it becomes vapor. The proportions of liquid and vapor can be changed at will by heating or cooling; but neither heating nor cooling (within certain limits) will cause a change in the temperature. When the enthalpy has been increased by 970 Btu over its value for the liquid at 212 F the entire mass will be in the vapor phase and further heating will result in a rise in temperature. The change in enthalpy between the liquid phase and the vapor phase at the same pressure and temperature is called the *latent heat of vaporization*. The liquid at 1 atmosphere of pressure and 212 degrees of temperature, from which the vapor was evaporated and with which the vapor can exist in all proportions in equilibrium, is an example of a *saturated liquid*. The vapor which is formed from the liquid and with which the liquid can exist in equilibrium is known as *saturated vapor*. Further heating will cause a rise in the temperature of the vapor which is then known as *superheated vapor*.

If the pressure exerted by the piston were 100 lb/sq in. abs instead of atmospheric pressure the ice would melt at a slightly lower temperature* and the liquid would evaporate at a higher temperature. The boundaries between phases for carbon dioxide are shown on a temperature-pressure plane in Fig. 17. This diagram shows that below a certain pressure the solid phase may exist in equilibrium with the vapor phase, or it may be converted to the vapor phase without passing through the liquid phase during the conversion.† Above that

* This is a peculiarity of water. Most substances have higher melting points at higher pressures as does water at pressures above 30,000 lb/sq in.

† This process is known as *sublimation* as distinguished from fusion (solid to liquid) and evaporation (liquid to vapor).

pressure the solid phase can exist in equilibrium with the liquid phase but not with the vapor phase. Thus the solid-vapor boundary meets

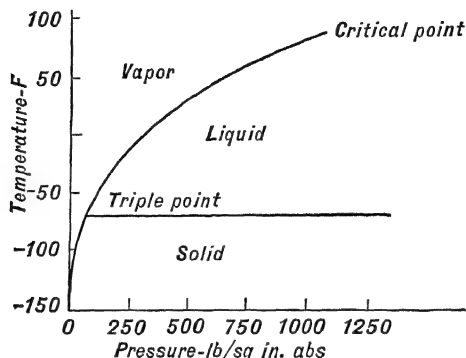


FIG. 17. Phase Boundaries for Carbon Dioxide

the solid-liquid boundary where the two join the liquid-vapor boundary. The junction of these curves corresponds to a state at which all three phases can coexist in equilibrium. It is called the *triple point*.

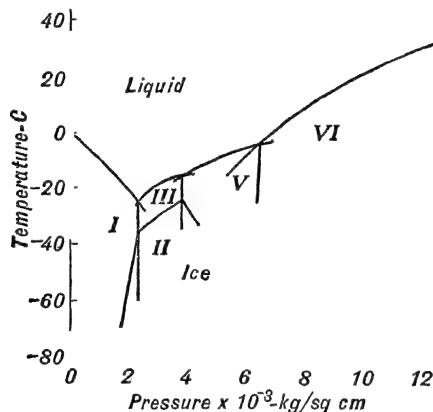


FIG. 18. Temperature-Pressure Diagram for Liquid and Solid Water

From Bridgman, *J. Franklin Inst.*, Vol. 177 (1914), pp. 315-332.

At the other extremity of the liquid-vapor boundary is the critical point beyond which there is no latent heat of vaporization and no other characteristic change which normally marks a change in phase.

Boundaries between liquid and solid phases of water are shown in Fig. 18. Bridgman* has determined the latent heats at these boundaries.

Because of the latent heats the phase boundaries which are lines on

* *Proc. Am. Acad.*, Vol. 47 (1912), pp. 441-558.

the temperature-pressure plane are bands or areas on the enthalpy-pressure plane (Fig. 19). They are areas on the pressure-volume

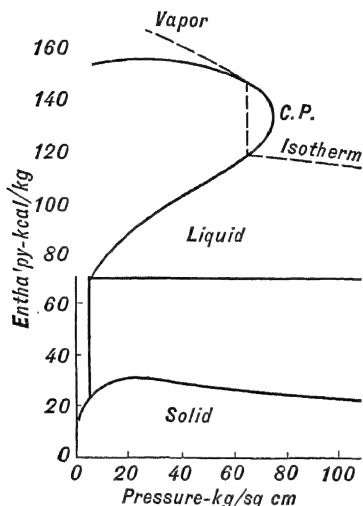


FIG. 19. Enthalpy-Pressure Diagram for Carbon Dioxide

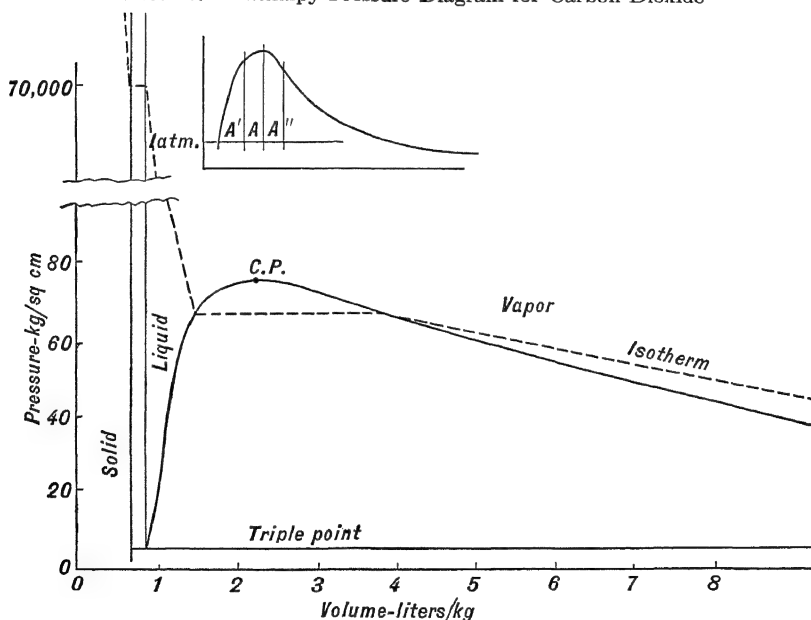


FIG. 20. Pressure-Volume Diagram for Carbon Dioxide

plane as well (Fig. 20) because marked changes in volume occur during the transition between phases, as is apparent when water evaporates.

Mixtures of Two Phases

There is a type of property used in thermodynamics the value of which for any system is equal to the sum of its values for all the parts of the system. We shall call such properties extensive properties. Volume, internal energy, and enthalpy are extensive properties. Pressure, temperature, and density, on the other hand, are not extensive properties. If r stands for the value of an extensive property for unit mass of a two-phase mixture, we may write that r is equal to the sum of the value of the property r for the liquid part of the system and the value of the property r for the vapor part of the system:

$$r = xr_g + (1 - x)r_f,$$

where x denotes the mass of vapor per unit mass of mixture; r_f , the magnitude of the property for unit mass of saturated liquid in the mixture; and r_g , the magnitude of the property for unit mass of saturated vapor in the mixture. Similarly for any other extensive property, r' , we have

$$r' = xr'_g + (1 - x)r'_f.$$

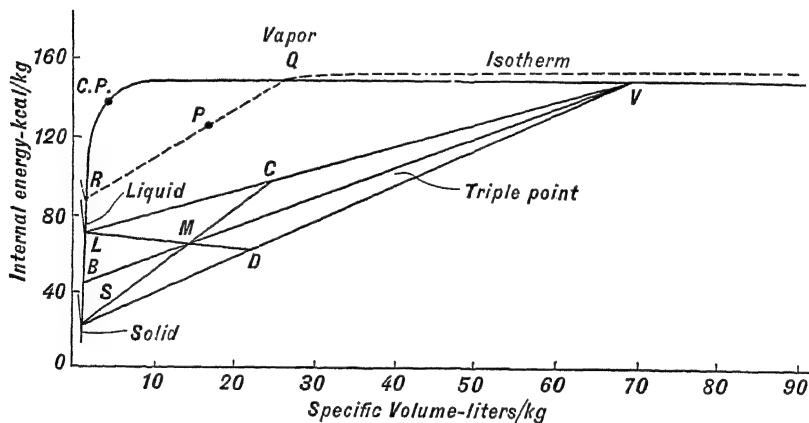


FIG. 21. Energy-Volume Diagram for Carbon Dioxide

The derivative of the first of these properties with respect to the second is given by

$$\frac{dr}{dr'} = \frac{dr/dx}{dr'/dx} = \frac{r_g - r_f}{r'_g - r'_f},$$

which is independent of x . Therefore, the line on a diagram of extensive properties (for example, Fig. 21) representing mixtures of two

phases in equilibrium at any one pressure and temperature is a straight line; and the proportions of the two phases in a mixture represented by a point on that line are given by the ratio of the lengths of the segments of the line on either side of the point. Thus, in Fig. 21, the point P represents a mixture in which the mass proportion of liquid to vapor is $PQ : RP$.

On the pressure-volume diagram and on the energy-volume diagram (Figs. 20 and 21) the mixtures of two phases at any pressure and temperature are represented by straight lines, each point on which represents particular proportions of the two phases and all points on which represent all possible proportions. On the temperature-pressure diagram (Fig. 17), on the other hand, mixtures of all proportions at any one temperature and pressure are represented by a single point. Therefore the properties pressure and temperature do not together define the state of a two-phase mixture. On page 19 it was pointed out that two *independent* properties adequately determine the state of a pure substance. Within the two-phase region, pressure and temperature cannot be altered independently of each other — any variation in temperature must result in the variation in pressure indicated by the liquid-vapor boundary (Fig. 17) and no other.

The Triple Point

The triple point appears as a triangular area on any diagram which has neither pressure nor temperature as a coordinate, such as Fig. 21 which has internal energy and volume as coordinates.* The three corners of the triangle represent the solid (S), the liquid (L), and the vapor (V) phases, respectively. A point B on the line SL represents a mixture of solid and liquid in which the proportions of solid to liquid are $BL : SB$. Similarly a point C on the line LV represents a mixture of liquid and vapor in the proportions $CV : LC$; and a point D on the line SV represents a mixture of solid and vapor in the proportions $DV : SD$. Any point M within the boundaries of the triangular area represents a mixture of solid, liquid, and vapor. If the straight line LM intersects boundary SV at D the ratio of solid to vapor in state M is $DV : SD$. The other proportions are given in similar fashion by the intersections B and C on the other two boundaries.

On the enthalpy-pressure diagram and on the pressure-volume diagram (Figs. 19 and 20) the triple point is represented by a straight line. On the temperature-pressure diagram (Fig. 17) it is only a point. Thus no pair of properties of which temperature or pressure is one suffices to define a triple-point state.

* The enthalpy-entropy diagram is an exception.

The Critical Point

The critical state may be observed by filling a quartz tube with the proper proportions of a liquid and its vapor and then heating the tube and its contents. If the proper proportions are present at atmospheric pressure before the tube is sealed (A in Fig. 20) the meniscus separating the two phases will remain near the middle of the tube until, as the critical pressure is approached, it becomes less distinct and finally disappears. If too much liquid is introduced (A'), the meniscus will rise to the top of the tube before the critical pressure is reached; if too little (A''), the meniscus will disappear at the bottom of the tube before the critical pressure is reached.

At pressures higher than the critical pressure the liquid can be heated

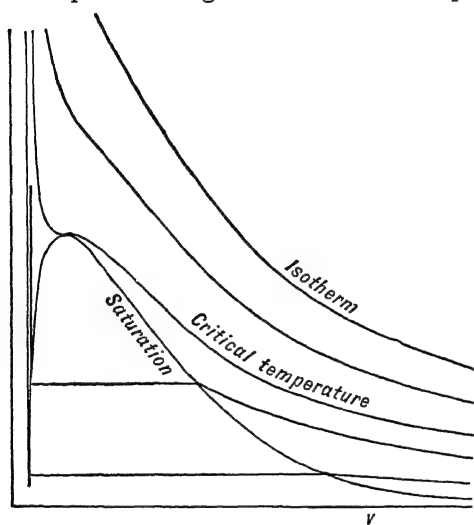


FIG. 22. Pressure-Volume Diagram

from a low temperature to a high one without any discontinuity in the process. Ebullition does not occur as at lower pressures, and no other event marks a change from the liquid phase to the vapor phase. The distinction between the two phases is therefore arbitrary.

At temperatures higher than the critical temperature the pressure of the vapor may be increased to very high values without any discontinuity in the process to mark a change to the liquid phase. The characteristics

of isotherms on a pressure-volume diagram at temperatures higher and lower than the critical temperature are illustrated in Fig. 22.

The Peabody Calorimeter

When the state of a system consisting of a gas or a liquid is to be determined the usual procedure is to measure the pressure and the temperature of the system, because these two properties can be readily measured and they are independent properties. But when the state of a system consisting of a mixture of liquid and vapor is to be determined, to measure the pressure and the temperature will not suffice, because these two are no longer independent properties. It is necessary, therefore, to measure some other property in addition to the pressure or the temperature.

The *Peabody calorimeter* is a device for determining the enthalpy of a mixture of liquid and vapor. A sample of the mixture is expanded in steady flow through a porous plug, an orifice, or some other throttling device into a large passage where its velocity is negligible. According to the energy equation of steady flow [6], for such an expansion the initial and final enthalpies must be identical. If the curve representing saturated vapor on the enthalpy-pressure diagram is similar in characteristics to that shown in Fig. 23 the expansion from the initial state *A* to a state *B* which is at lower pressure (though at the same enthalpy) may result in a single-phase state at *B*. Measurement of pressure and temperature on the low-pressure side of the throttling device will identify the state *B*, and a table of properties of the superheated vapor will yield the corresponding enthalpy. This is the enthalpy of state *A*.

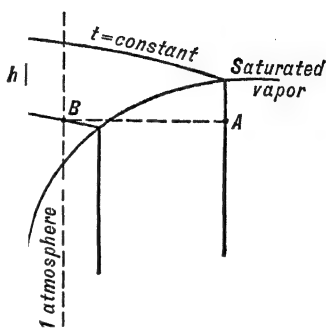


FIG. 23. End States in the Peabody Calorimeter

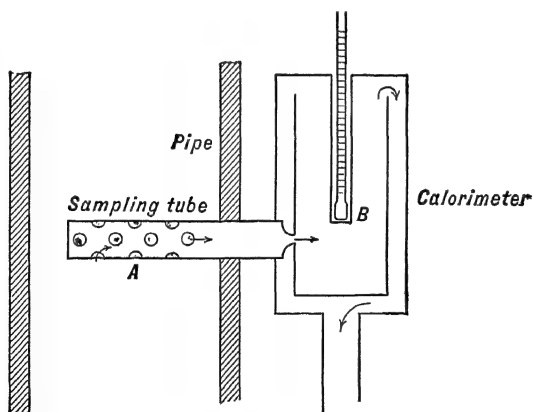


FIG. 24. Installation of a Peabody Calorimeter

In Fig. 24 is shown diagrammatically an installation of a jacketed Peabody calorimeter for sampling a mixture of vapor and liquid from a vertical pipe.

The Peabody calorimeter has certain limitations: Its indication is no better than the sample it receives; if the sample is different, in the pro-

portions of the two phases, from the stream that is to be measured, then the indication will be in error. The state *B* (Fig. 23) must be a vapor state; that is, the enthalpy of the mixture must be greater than that of the saturated vapor corresponding to the lower pressure. This requirement limits the use of the calorimeter to small proportions of liquid and to pressures that are low relative to the critical pressure.

Tables of Properties

The determination of the properties of substances has been the object of scientific experiment and analysis since the beginnings of science. Some concept of the magnitude of the accumulation of data on properties can be obtained by an inspection of the *International Critical Tables*,* which are a compilation in seven volumes of significant data in extremely abbreviated form.

Similar data have been expanded, for a few substances commonly employed in engineering and science, into extensive tables showing the values of many properties in a form dictated by utility and convenience. Thus, there are tables of the thermodynamic properties (that is, properties commonly used in the applications of thermodynamics) of water, ammonia, carbon dioxide, ammonia-water mixtures, etc.†

The properties of water are known with precision over a wider range than are the properties of any other substance. Moreover, water is employed in engineering and science perhaps more commonly than any other substance. For these reasons its properties have been tabulated in great detail.

The volume entitled *Thermodynamic Properties of Steam, including data on the liquid and solid phases*, by Keenan and Keyes, is an example of a table of properties of water which was prepared primarily to fill the needs of the engineer. It consists principally of tabulations of certain properties which have been defined above, namely, specific volume, enthalpy,‡ and (in some places) internal energy, and another

* *International Critical Tables*, McGraw-Hill, 1926.

† The following are examples:

Water, Keenan and Keyes (Wiley, 1936).

Koch (Springer, 1938).

Callendar (Arnold, 1939).

Dorsey (Reinhold, 1940).

Ammonia (Bureau of Standards, 1924).

Carbon dioxide, Quinn and Jones (Reinhold, 1936).

Ammonia-water mixtures, Jennings and Shannon, *Refrig. Eng.*, Vol. 35 (1938), pp. 333-336.

‡ The engineer prefers a tabulation of enthalpy to a tabulation of internal energy because the bulk of his problems relate to steady-flow processes. Where the internal energy is not tabulated it can be obtained readily from the relation $u = h - pv$.

property, entropy, which is defined in subsequent pages. The values of these properties are given for various combinations of values of the independent properties, pressure and temperature. The ranges of states covered by the various tables are shown in Fig. 25, where the numbers refer to correspondingly numbered tables.

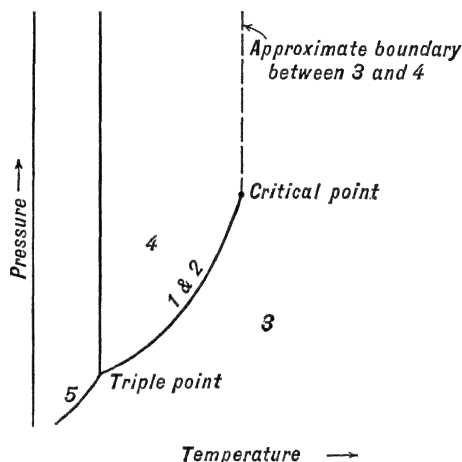


FIG. 25. The Ranges of States Covered by Tables 1, 2, 3, 4, and 5 in the Steam Tables of Keenan and Keyes

Tables 1, 2, and 5 are tables of saturation states, and these have therefore a single independent argument, namely, temperature in Tables 1 and 5 and pressure in Table 2. Some sample lines from Table 2 are given below:

Table 2. Saturation: Pressures

Abs. Press. Lb. Sq. in.	p	t	Specific Volume			Enthalpy			Entropy			Internal Energy		
			v_f	v_g		Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Evap. s_{fg}	Sat. Vapor s_g	Sat. Liquid u_f	Evap. u_{fg}	Sat. Vapor u_g
50	281.01	0.01727	8.515			250.09	924.0	1174.1	0.4110	1.2474	1.6585	249.93	845.4	1095.3
51	282.26	0.01728	8.359			251.37	923.0	1174.4	0.4127	1.2442	1.6569	251.21	844.3	1095.5
52	283.49	0.01729	8.208			252.63	922.2	1174.8	0.4144	1.2409	1.6553	252.46	843.3	1095.8
53	284.70	0.01730	8.062			253.87	921.3	1175.2	0.4161	1.2377	1.6538	253.70	842.4	1096.1
54	285.90	0.01731	7.922			255.09	920.5	1175.6	0.4177	1.2346	1.6523	254.92	841.5	1096.4

Table 3 has two independent arguments, pressure and temperature, and three dependent quantities, specific volume, enthalpy, and entropy. Some sample lines follow:

Table 3. Superheated Vapor

Abs. Press. Lb./Sq. in. (Sat. Temp.)		Temp.	Temperature—Degrees Fahrenheit											
			290°	300°	320°	340°	360°	380°	400°	420°	440°	460°	480°	500°
(283.49)	s	0.017	8.208	8.293	8.423	8.580	8.732	8.881	9.027	9.171	9.314	9.454	9.591	9.726
		252.6	1174.8	1178.1	1183.5	1194.3	1204.7	1214.8	1224.8	1234.8	1244.6	1254.3	1264.2	1274.0
		0.4144	1.6553	1.6601	1.6672	1.6809	1.6940	1.7066	1.7186	1.7303	1.7417	1.7527	1.7635	1.7739
(284.70)	h	0.017	8.062	8.131	8.259	8.511	8.759	9.004	9.245	9.485	9.723	9.960	10.195	10.429
		253.9	1175.2	1178.1	1183.5	1194.1	1204.5	1214.6	1224.7	1234.6	1244.5	1254.3	1264.1	1273.9
		0.4161	1.6538	1.6577	1.6648	1.6786	1.6917	1.7043	1.7164	1.7281	1.7395	1.7505	1.7613	1.7718
(285.90)	h	0.017	7.922	7.974	8.100	8.348	8.592	8.833	9.071	9.306	9.540	9.772	10.103	10.233
		255.1	1175.6	1177.8	1183.2	1193.9	1204.3	1214.4	1224.5	1234.5	1244.4	1254.2	1264.0	1273.8
		0.4177	1.6523	1.6553	1.6625	1.6763	1.6894	1.7021	1.7142	1.7259	1.7373	1.7483	1.7591	1.7696

Table 4 is like Table 3 in the arrangement of the arguments, but the nature of the dependent quantities has been altered in order to reduce the dimensions of the table. Instead of the specific volume Table 4 gives the excess of the specific volume over the saturation specific volume at the temperature in question. Corresponding constant-temperature differences are given instead of the enthalpy and the entropy. Sample lines follow:

Table 4. Compressed Liquid

		Temperature—Degrees Fahrenheit											
		32°	100°	200°	300°	400°	500°	600°	620°	640°	660°	680°	
Abs. Press. Lb./Sq. In. (Sat. Temp.)	Saturated	p	0.08854	0.9492	11.526	67.013	247.31	680.8	1542.9	1786.6	2059.7	2365.4	2708.1
	Liquid	v_f	0.016022	0.016132	0.016634	0.017449	0.018639	0.020432	0.023629	0.024466	0.02598	0.02777	0.03054
		h_f	0	67.97	167.99	269.59	374.97	487.82	617.0	646.7	678.6	714.2	757.3
		s_f	0	0.12948	0.29382	0.43694	0.56638	0.68871	0.8131	0.8398	0.8679	0.8987	0.9351
200 (331.79)	$(v - v_f) \cdot 10^5$		-1.1	-1.1	-1.1	-1.1							
	$(h - h_f)$		+0.61	+0.54	+0.41	+0.23							
	$(s - s_f) \cdot 10^3$		+0.03	-0.05	-0.21	-0.21							
400 (444.59)	$(v - v_f) \cdot 10^5$		-2.3	-2.1	-2.2	-2.8	-2.1						
	$(h - h_f)$		+1.21	+1.09	+0.88	+0.61	+0.15						
	$(s - s_f) \cdot 10^3$		+0.04	-0.16	-0.47	-0.56	-0.40						
4000	$(v - v_f) \cdot 10^5$		-21.5	-19.2	-21.0	-27.5	-40.0	-64.5	-132.2	-160	-202	-270	-400
	$(h - h_f)$		+11.88	+10.49	+9.03	+7.41	+4.71	-0.16	-10.0	-13.3	-17.4	-22.5	-32.4
	$(s - s_f) \cdot 10^3$		+0.29	-2.42	-4.74	-6.77	-9.40	-13.03	-19.3	-21.4	-24.0	-27.2	-34.3
4500	$(v - v_f) \cdot 10^5$		-24.1	-21.4	-23.5	-30.7	-44.9	-72.5	-151.5	-184	-234	-313	-464
	$(h - h_f)$		+13.32	+11.80	+10.15	+8.40	+5.40	+0.02	-11.1	-15.1	-19.9	-26.4	-38.4
	$(s - s_f) \cdot 10^3$		+0.26	-2.74	-5.33	-7.60	-10.58	-14.80	-22.4	-25.1	-28.3	-32.7	-41.8

In order to obtain the properties for a state intermediate between the states tabulated it is only necessary to interpolate in Table 4 (linear interpolation is generally adequate) for the differences from the saturation values. The saturation values themselves can best be obtained from Table 1, unless the temperature corresponding to the state appears at the head of one of the columns of Table 4, whereupon the saturation values may also be found at the head of the column. For purposes of interpolation at low pressures it should be noted that the value of each of the differences — $(v - v_f)$, $(h - h_f)$, and $(s - s_f)$ — becomes zero at the saturation pressure corresponding to each temperature.

PROBLEMS

1. From the *Steam Tables*, tabulate pressure, temperature, specific volume, enthalpy, and internal energy for:

- Saturated liquid at 1 standard atmosphere pressure.
- Saturated vapor at 1 standard atmosphere pressure.
- Vapor superheated 100 degrees at 1 standard atmosphere.
- Liquid at 100 F and 1 standard atmosphere.

2. Tabulate: (a) the latent heat of vaporization, (b) the change in volume during vaporization, (c) the increase in internal energy during vaporization, for H_2O at 100, 300, 500, 700, and 705.4 F.

3. Complete the following table for H_2O , entering either numerical results or dashes in each block as the item may or may not be pertinent.

State number	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	<i>j</i>
Mass, pounds	3	4		2				1	10	1
Total volume, cu ft			40	4	626	340	50			0.01764
Specific volume					200					
Pressure, gage		90					100			
Pressure, abs	85		200	200				250	2000	
Temperature, F			500			185			100	350
Superheat, F		80								
Quality (dryness)	0.80				1.00	1.00	0.80	0.01		
Per cent moisture										

4(a) Find the proportions by volume of liquid and vapor H_2O in a sealed tube at atmospheric pressure that will pass through the critical state when heated. Assume no change in volume.

(b) How much heat must be added to the contents of the tube between atmospheric pressure and the critical state if the volume enclosed is 1 cu in.?

5. A mixture of ice, liquid water, and water vapor is in equilibrium in an insulated rigid container. The mixture is stirred by a paddle wheel until only vapor remains in the container at a pressure of 200 lb/sq in. abs and a temperature of 381.8 F.

(a) What were the mass proportions of liquid and vapor in the container when the last of the ice had just melted?

(b) How much stirring work per pound of contents was done between the time the last piece of ice melted and the time the last drop of water evaporated?

TRIPLE-POINT DATA

Temperature, 32.02 F; pressure, 0.0888 lb/sq in. abs

	Enthalpy Btu/lb	Specific volume cu ft/lb
Solid	-143.3	0.01747
Liquid	0.02	0.01602
Vapor	1075.8	3303.

6(a) From the triple-point data given above determine how much the increase in enthalpy exceeds the increase in internal energy for a pound of ice melting to liquid at the triple point.

(b) How much work is done by a pound of ice if it melts under a piston at triple-point conditions?

7. A steady stream of steam at 3 lb/sq in. gage pressure, superheated 60 F, is condensed in a radiator and is trapped out at 150 F. How much heat is given up by each pound of steam? Barometer is 30.55 in. of Hg (0 C).

8. Ten pounds of steam at 150.3 lb/sq in. gage pressure with 2 per cent moisture is condensed every minute in the jackets of a reciprocating engine. The condensate leaves the jacket at the temperature of the steam. How much heat is given up by the jacket steam per minute?

9. A steam main closed at both ends has an internal volume of 43.22 cu ft which is filled with dry saturated steam at 280 F.

- (a) How much heat must flow from the steam to reduce the quality to 0.5?
- (b) What will be the pressure in the main when the quality is 0.5?

10. Measurements taken during a test of a reciprocating engine indicate that at two points during a revolution of the crankshaft the volumes occupied by steam between the piston and the valve are 0.70 and 1.36 cu ft respectively. The corresponding pressures in the cylinder are 100 lb/sq in. gage and 50 lb/sq in. gage. At both points 0.2 lb of steam are confined within cylinder and ports.

- (a) Find the temperature of the steam at each point.
- (b) If 7600 ft-lb of work is done on the piston between these two points, how much heat is transferred between steam and cylinder walls, and in which direction?

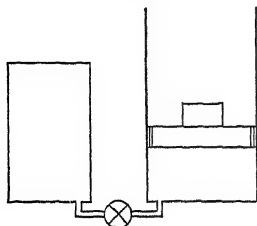
11. A steam turbine receives 20,000 lb of steam per hour at a pressure of 80 lb/sq in. abs and at negligible velocity. The power delivered by the steam to the turbine shaft is 1325 kw. The steam leaves the turbine at 2 in. Hg abs carrying 10 per cent moisture and traveling at 1000 ft/sec. The condensate leaves the condenser as saturated liquid at condenser pressure and at negligible velocity.

- (a) Find the temperature of the steam approaching the turbine.
- (b) How much heat is delivered to the condenser cooling water per hour?
- (c) If the cooling water rate of flow is 800,000 lb/hr and its inlet temperature is 60 F, what is its discharge temperature?

12. A throttle valve reduces the pressure of steam as it flows through a pipe line from 150 lb/sq in. abs to 50 lb/sq in. abs. The superheat is 10 degrees before the throttle valve where the velocity is low. Some distance after the throttle valve the stream fills the pipe and proceeds at negligible velocity. Find the temperature and superheat of the steam there. Assume negligible heat loss from the pipe.

13. In a Peabody calorimeter steam is expanded through an orifice into a large chamber at about atmospheric pressure where it slows down to low velocity. A test with a Peabody calorimeter gives a temperature of 250 F in the large chamber in which the pressure is 0.6 in. Hg above atmospheric pressure. If the pressure in the steam main from which the steam is sampled is 100 lb/sq in. abs, find the quality of the steam in the main.

14. An exhausted chamber with non-conducting walls is connected through a valve with a steam main through which steam at 100 lb/sq in. abs and 500 F is flowing. The valve is opened and steam flows into the chamber until the pressure within the chamber is 100 lb/sq in. abs. Find the temperature of the steam in the chamber when flow stops. Define your system to include only the steam which is finally in the chamber, and inspect the boundaries of the system for work.



15. A chamber contains 1 lb of steam at a pressure of 300 lb/sq in. abs and at a temperature of 700 F. It is connected through a valve with a vertical cylinder which is closed on top by a piston. The piston is loaded by a weight of such magnitude that a pressure of 100 lb/sq in. abs is necessary to support the piston.

Initially the piston is at the bottom of the cylinder and the volume confined between valve and piston is

negligible. The valve is opened slightly, and steam flows into the cylinder slowly until the pressures on the two sides of the valve are equalized.

The final temperature in the chamber is found to be 439 F. Find the final temperature in the cylinder. Assume no heat transfer from steam to walls or from chamber to cylinder. Assume also that the state of the steam in the cylinder is finally homogeneous.

SYMBOLS

h	enthalpy per unit mass
p	pressure
r	value of an extensive property per unit mass
s	distance
u	internal energy of unit system in the absence of motion, gravity, etc.
v	specific volume
x	mass of vapor per unit mass of mixture

SUBSCRIPTS

f	final, saturated liquid
g	saturated vapor

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CHAPTER VI

THE SECOND LAW OF THERMODYNAMICS

Heat Engines

A *heat engine* may be defined as a *continuously operating system across whose boundaries flow only heat and work*. It may be used to deliver work to external devices, or it may receive work from external devices and cause heat to flow from a low level of temperature and to a high level of temperature. This latter type of heat engine is known as a refrigerator.

Our definition requires that the material which constitutes the heat engine must execute only cyclic changes. Otherwise the system would not operate continuously but would have to be replaced by new material at intervals.

A simple type of heat engine (Fig. 26a) consists of a cylinder on end closed at the top by a freely moving piston which confines a quantity of air. The piston supports a platform which comes to level *A* when the piston rests on stops near the bottom of the cylinder and comes to level *B* when it is up against stops at the top of the cylinder. Assume that the piston is initially at the lower position and a weight *G* is slid onto the platform. A heat source *S* is now brought into contact with the bottom of the cylinder and the resulting flow of heat to the confined air

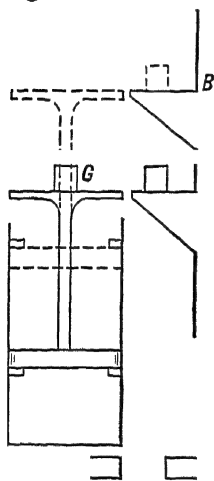


FIG. 26a

causes its pressure to rise until the piston is lifted off the lower stops. The heating may be continued until the piston comes up against the top stops when the weight may be slid off onto level *B*. Next, the heat source is removed and in its place is put a low-temperature body or heat sink *Z*. The direction of heat flow is now reversed and the pressure of the confined air falls until it is just enough to support the weight of the piston and its platform. The piston descends upon further cooling until it comes to its original position against the lower stops. The complete cycle of events may be repeated without renewing any part of the engine or its working fluid, provided only that the source and sink

are continuously available at the desired temperatures. In Fig. 26b the cyclic process which the working fluid experiences is shown on the pressure-volume and temperature-volume diagrams.

For this cycle we may re-write the First Law [1a] in the form

$$W = q_1 - q_2,$$

where W denotes the net work done by the air during a complete cycle, q_1 the heat received from the source, and q_2 the heat rejected to the sink.

It is customary to define the *efficiency of a heat engine*, which we shall denote by η , as the ratio of the work delivered to the heat received from the source: thus,

$$\eta = \frac{W}{q_1} = \frac{q_1 - q_2}{q_1}.$$

For the air engine just described the efficiency is less than unity because q_2 stands for a positive number.

The Carnot Engine

A heat engine can be devised in which the working fluid receives all heat at one temperature and rejects all heat at one other temperature, as follows. A cylinder containing a quantity of air confined by a piston is brought into good thermal contact with large *heat reservoir** S at temperature t_1 (Fig. 27). When thermal equilibrium is established the following processes are executed:

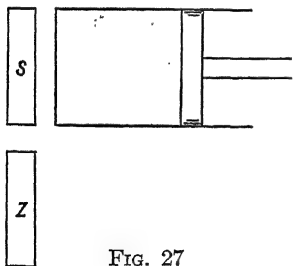


FIG. 27

1-2. With the fluid in state 1 (Fig. 28), the heat source is removed from the cylinder so that the fluid is thermally isolated and the piston is allowed to move out slowly to position 2. During this operation both the pressure and the temperature will fall.

When the temperature reaches that of a second large heat reservoir Z at t_2 , the motion of the piston is stopped.

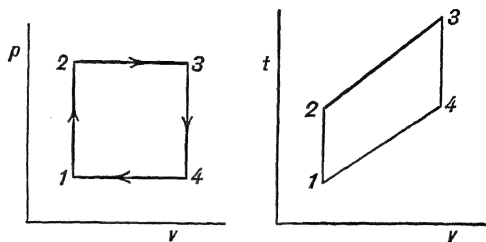


FIG. 28b

* The term reservoir is used here to mean a heat source or a heat sink of uniform temperature. It should not be inferred from the more general definition of the term that heat can be stored. When heat is received from a reservoir the internal energy of the system which constitutes the reservoir is reduced.

2-3. The reservoir, Z is now brought into good thermal contact with the cylinder and the piston is made to move back toward its original position so slowly that the air remains at the temperature of the reservoir. At any pressure during this compression the temperature and volume of the air will be less than at the same pressure during the expansion 1-2 because of the flow of heat out to the sink.

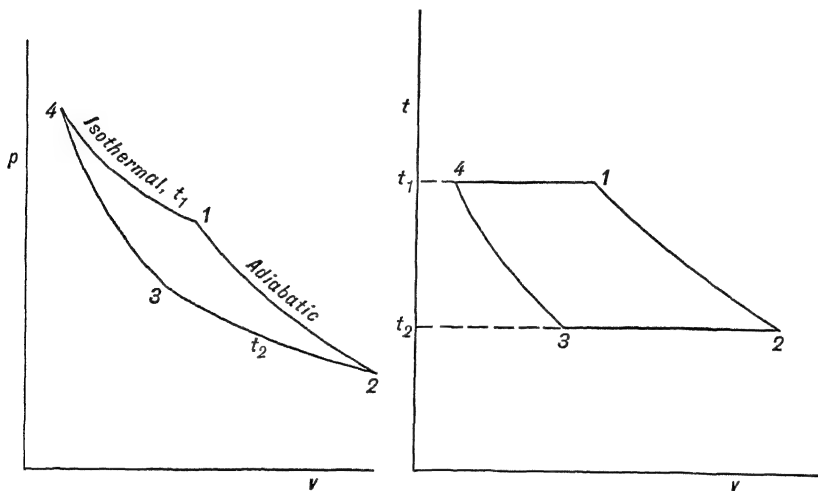


FIG. 28. The Carnot Cycle

3-4. When the piston reaches point 3 the reservoir Z is removed so that the air is thermally isolated once more, and the compression is continued. Without the cooling action of the reservoir the temperature will rise. When it reaches t_1 again the piston is stopped.

4-1. The cylinder is brought into good thermal contact with the reservoir S and the piston is allowed to move outward so slowly that the air remains at the temperature of the reservoir. When the air reaches its original volume and state the cycle is completed.

Now the adiabatic expansion 1-2 may be executed again and the cycle repeated as often as desired.

This is an example of a *Carnot cycle*, which may be described as consisting of two isothermal processes connected by two adiabatic processes.

A characteristic of the Carnot cycle is its reversibility. All its processes can be performed in the reverse direction and in the reverse order as shown below.

During any infinitesimal movement of the piston from a to b through a displacement δv (Fig. 29) in process 1-2, the work done by the fluid is $p \delta v$ (see page 25).

If at b the piston is stopped and caused to move back to a again, the work done by the air is $-p \delta v$ (δv being a positive number). For any adiabatic process the increase in internal energy is given, in accordance with [2], by

$$du = -dW.$$

Therefore the change in internal energy of the fluid as the piston moves from a to b will be canceled by the change in internal energy when the piston returns from b to a . Both the volume and the internal energy of the fluid will be the same after the excursion aba as before; consequently, the state of the fluid will be the same before and after.

If this reasoning is applied to the entire process 1-2 it becomes evident that the expansion can be reversed starting at state 2 and returning to state 1 at the expense of a quantity of work exactly equal to the work of expansion from 1 to 2.

During any infinitesimal movement of the piston from a' to b' through displacement δv while the fluid is in temperature equilibrium with the heat source S (process 4-1), the work done by the fluid is $p \delta v$ and the heat transferred to it is

$$dQ = du + dW,$$

where dW is identical with $p \delta v$. If at b' the piston is stopped and caused to move back again to a' while maintaining temperature equilibrium with S , the state of the fluid at a' will be the same as before the excursion because the temperature and the volume are both the same as before. Consequently the internal energy will be the same as before and we may write

$$du(a' \text{ to } b') = -du(b' \text{ to } a').$$

It is also true that

$$dW(a' \text{ to } b') = p \delta v = -dW(b' \text{ to } a').$$

Therefore, we get

$$dQ(a' \text{ to } b') = -dQ(b' \text{ to } a').$$

Applying this reasoning to the entire process 4-1 we find that the constant-temperature expansion can be reversed starting at state 1 and

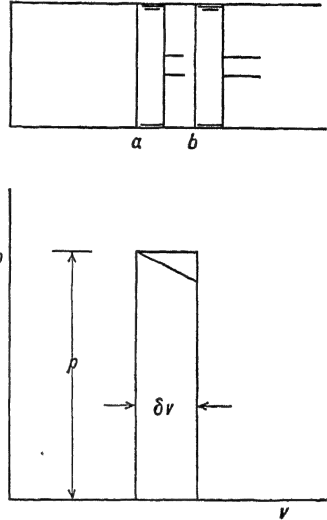


FIG. 29

returning to state 4 at the expense of a quantity of work exactly equal to the work of expansion from 4 to 1, and accompanied by a heat flow to S exactly equal to the heat flow from S during the expansion.

Similarly processes 2–3 and 3–4 and, consequently, the entire Carnot cycle can be shown to be reversible. In the original operation heat was received from S at high temperature, work was delivered to the piston, and heat was rejected to Z at low temperature. In the reversed operation heat is received from Z at low temperature, work is received from the piston, and heat is delivered to S at high temperature. This is the cycle of the Carnot heat pump or refrigerator.

It should be noticed that when the engine of Fig. 26*a* is reversed it will not act as a heat pump between the sink and source indicated.

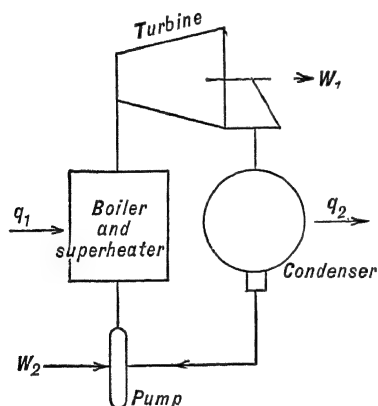


FIG. 30. A Steady-Flow Engine

The Steady-Flow Engine

The most familiar example of a steady-flow engine is that shown in Fig. 30. It consists of a closed circuit in which liquid is evaporated as it receives heat q_1 in the boiler, the vapor formed is expanded to lower temperature as it delivers work W_1 to a shaft in the turbine, the vapor condenses at low temperature and rejects heat q_2 to cooling water in the condenser, and the condensate receives work W_2 from the pump as it is returned to the boiler.

Efficiency of Heat Engines and Perpetual Motion of the Second Kind

The efficiency η of a heat engine was defined on page 59 by the equation

$$\eta = \frac{W}{q_1} = \frac{q_1 - q_2}{q_1}.$$

In each of the engine cycles described above, the value of this ratio is less than unity because q_2 is in each instance greater than zero; that is, only part of the heat received is converted into work, the remainder being rejected to the heat sink. In fact, in these cycles a finite rejection of heat occurs regardless of how perfectly and frictionlessly the processes of the cycle are carried out.

It is important to know how nearly one could obtain complete conversion of heat into work, or how nearly one could realize an efficiency of unity, by improvement of an engine or its cycle. This question will

be answered quantitatively on subsequent pages through the Second Law of Thermodynamics and a new scale of temperature. In the approach to that answer it is necessary first to show that if a heat engine could be devised which would completely convert into work all the heat it received at any one level of temperature, then work could be continuously produced at the expense only of heat taken from the atmosphere, the rivers, the ocean, or the solid earth.

Assume that a heat engine can be devised (E , Fig. 31) which will take heat from a reservoir at some finite temperature t_1 and deliver an equal amount of work. Let a heat pump P (for example, a Carnot heat pump) be provided to deliver to that reservoir an amount of heat q_1 , equal to the heat required by the engine. Then the reservoir will serve merely as a conductor between the pump and the engine. The heat pump may use the atmosphere, a river, the ocean, etc., at a temperature t_2 as a source from which it obtains a lesser quantity of heat q_2 . The work necessary to its operation, $W_p = q_1 - q_2$, can be obtained from the work of the engine. There remains a net output of work from the combination

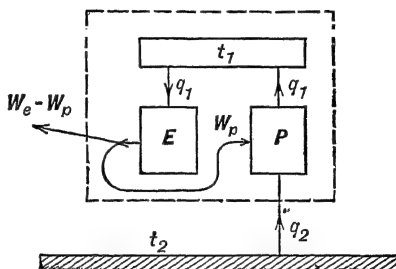


FIG. 31

$$W_n = W_E - W_P = q_1 - (q_1 - q_2) = q_2.$$

The combined engine and pump will produce from a given amount of heat taken from a free and limitless source an equal amount of work. No expensive, high-temperature supply of energy is needed.

Such an engine would be, without question, the most profitable engine ever devised. It should be noticed, however, that it is not a perpetual-motion machine of the ordinary kind, because a perpetual-motion machine is a device which continuously produces work without drawing upon any supply of matter or heat. This machine, on the other hand, receives heat as it produces work. Nevertheless, it is in no way less desirable than a perpetual-motion machine, because the supply of heat is free and abundant.

In fact, in some respects it might be considered more desirable than a perpetual-motion machine. For, if we were to substitute for the atmosphere, which serves as the source of heat, some object that we wished to cool below the temperature of its environment, this machine would cool it and produce work and leave no other effects. Thus, our machine would produce work and refrigeration simultaneously at no expense,

whereas a perpetual-motion machine would produce only work. It has come to be known as a *perpetual-motion machine of the second kind*.

The Second Law of Thermodynamics

The Second Law of Thermodynamics states that a perpetual-motion machine of the second kind is an impossibility. Following Planck,* and using the term *reservoir* to denote a system whose temperature is uniform, we shall restate it as follows: *It is impossible to construct an engine which will work in a complete cycle and produce no effect except to raise a weight and exchange heat with a single reservoir.*

Since it derives from no other scientific principle, the Second Law, like the First Law, is justified only by the failure of all attempts to disprove it. For disproof it is not necessary to construct a perpetual-motion machine of the second kind; it is necessary only to refute any one of the numerous corollaries of the law. Since each advance made in the precision of experimental science has served to confirm all these corollaries, the Second Law is now as firmly established as the First Law.

PROBLEMS

1. Starting with 1 lb of liquid water at 65 F under a weightless piston exposed to the atmosphere (15 lb/sq in.):

- (a) Describe the cycle of processes and the states passed through by the H_2O as it lifts weights through a height of 4.8 in. on the piston as described on pages 58 and 59. The piston area is 1 sq ft and the weight lifted each cycle is 143 short tons.
- (b) Find the heat transferred in each of the processes which constitute the cycle.
- (c) What is the thermal efficiency of the engine?

Answer the questions in the preceding problem for an initial water quantity of 2 lb, other conditions being the same.

2. A freak engine receives heat and does work on a slowly moving piston at such rates that the cycle of operations of a pound of the working fluid can be represented as a circle 2 in. in diameter on a p - v diagram on which 1 in. = 100 lb/sq in. and 1 in. = 2 cu ft/lb.

- (a) How much work is done by each pound of the working fluid for each cycle of operations?
- (b) If the heat rejected by the engine to a cold reservoir is 1000 Btu/cycle/lb of working fluid, what is the thermal efficiency of the engine?

3. A cylinder containing 2.5 lb of steam is closed by a slowly moving piston traveling back and forth between two extreme positions. At one of these extreme positions the volume available to the steam is 5 cu ft/lb; at the other it is 20 cu ft/lb. During the progress of the piston from one extreme position to the other, heat flows to or from the steam at such a rate as to keep the temperature of the steam constant. With the piston at either end, heat flows to or from the steam so that the temperature changes between the two constant temperatures while the piston is stationary.

* *Treatise on Thermodynamics*, by Max Planck, translated by Alexander Ogg, p. 89. Longmans, Green and Company, 1927.

If the higher temperature is 500 F and the lower is 300 F, find:

- (a) The work per cycle.
- (b) The thermal efficiency of the heat engine.

4. In a steady-flow steam cycle the fluid flows in turn through a feed pump, boiler, turbine, condenser, and back to the feed pump. The conditions of the fluid between these various pieces of apparatus are as indicated below:

	Pressure lb/sq in. abs	Temperature or Quality	Velocity ft/sec
Pump	300	80°	20
Boiler	295	600°	150
Turbine	1	91%	1000
Condenser	1	80°	20
Pump			

Find the thermal efficiency of this steady-flow engine, neglecting heat loss from the apparatus and change in level from point to point.

5. The thermal efficiency of a certain engine is 30 per cent; find:

- (a) The heat transferred to the engine per kilowatt-hour of work delivered.
- (b) The ratio of heat received to heat rejected.
- (c) The ratio of work done to heat rejected.

6. A storage battery connected to an electric motor constitutes an engine which can raise a weight and take a *negative* amount of heat from a single source, the atmosphere. Why isn't this a violation of the Second Law?

SYMBOLS

q	a positive number representing a quantity of heat
Q	heat to system
t_1, t_2	temperatures of source and sink respectively
u	internal energy of unit system in the absence of motion, gravity, etc.
v	specific volume
W	work from system

GREEK LETTER

η	efficiency of heat engine
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SUBSCRIPTS

E	heat engine
n	net output
p	pump

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CHAPTER VII

REVERSIBILITY

The Definition of a Reversible Process

The concept of reversibility has been discussed briefly above in connection with the Carnot cycle. Here we shall consider it in more detail because it plays so large a part in the development of the corollaries of the Second Law.

A process is called reversible if the system and all elements of its environment can be completely restored to their respective initial states after the process has occurred.

It was shown on page 60 that the adiabatic process 1-2 of the Carnot cycle can be reversed in direction and the system can be restored to its initial state 1 by returning to it precisely the amount of work received from it in the direct process 1-2. If the work of process 1-2 had been used to accelerate a frictionless flywheel, then in the reversed process 2-1 the system would be restored to its initial state and the flywheel to its initial velocity. Thus, all traces of the original process would be effaced. Therefore, the processes 1-2 and 2-1 are reversible processes in accordance with the definition given above.

It was shown on page 61 that the isothermal process 4-1 can be reversed with reversal of the work and of the heat. Thus, by reversing the process, the system, the flywheel, and the heat source S could all be restored to their respective states. Therefore, the processes 4-1 and 1-4 are reversible processes.

Since each part of the Carnot cycle is reversible — that is, the traces of each part can be completely effaced — the entire cycle must be reversible. In the direct cycle heat flows out of a reservoir at high temperature, a smaller amount of heat flows into a reservoir at low temperature, and work is delivered. By reversing the cycle the same quantity of work may be absorbed while quantities of heat that are identical in magnitude to those of the direct cycle, though reversed in direction, are transferred between the system and the reservoirs.

Some Irreversible Processes

We shall show with the aid of the Second Law that no process is reversible which involves (a) *friction*, (b) *transfer of heat across a finite interval of temperature*, or (c) *unrestrained expansion to lower pressure*:

(a) An example of a change of state involving friction is the change in a viscous fluid system at constant volume resulting from rotation of a paddle wheel in the fluid. The only effects of this process are a rise in the temperature of the fluid and the fall of a weight which causes the paddle wheel to rotate (Fig. 32).

Assume the process to be reversible. Then by the definition of a reversible process it must be possible to cool the fluid to its original temperature, raise the weight to its original position, and leave no other effects.

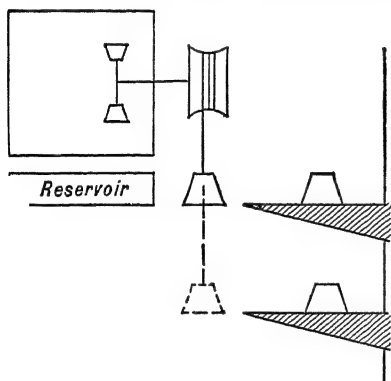


Fig. 32

Now the fluid can always be raised in temperature at constant volume by supplying heat from a reservoir that is higher in temperature than the fluid. After the heating we may employ the reversed paddle-wheel process to cool the fluid and raise a weight. We may supply heat from the reservoir, raise a second weight, and so on. But this device, which would be a consequence of the reversibility of the paddle-wheel process, is a perpetual-motion machine of the second kind and is, by the Second Law, an impossibility.

Therefore, the paddle-wheel type of process is irreversible.

(b) Transfer of heat across a finite interval of temperature from one reservoir (the hot reservoir) to another (the cold reservoir) would result in a decrease of a certain amount in the internal energy of the hot reservoir and an increase of the same amount in that of the cold reservoir. (It is assumed for convenience that the volumes occupied by the reservoirs are invariable.) If this process were reversible then a process could be found which would result in an increase in the internal energy of the hot reservoir and a decrease of equal amount in the internal energy of the cold reservoir. There would be no other effects.

A heat engine could be made to operate between these two reservoirs. After each withdrawal of heat from the hot reservoir the reverse process described above could be used to restore the internal energy of the hot reservoir to its initial value. To make the production of work continuous it would only be necessary to supply to the cold reservoir from a single source a quantity of heat equal to the work delivered by the engine. The engine in combination with the hot and cold reservoirs would then constitute a perpetual-motion machine of the second kind. Therefore, any process involving transfer of heat across a finite interval of temperature is irreversible.

(c) Unrestrained expansion of a fluid (as in the partition experiment of page 23) results in an increase in volume, a decrease in pressure, and no change in internal energy. If this process were reversible then a process could be found which would result in a decrease in volume, an increase in pressure, and no change in internal energy. There would be no other effects.

After the execution of this latter process the fluid could be expanded behind a piston so that work could be delivered to the surroundings. An amount of heat equal to the work could be supplied from a single source, so that the internal energy would be the same after the increase in volume as before. Thus, a cycle is described consisting of the reversed process of the preceding paragraph, expansion behind a piston, and heating. The result is a perpetual-motion machine of the second kind. Therefore, unrestrained expansion of a fluid is irreversible.

In problem 1 at the end of this chapter a number of processes are to be proved either reversible or irreversible. The examples given above will serve as patterns of the type of reasoning to be employed. In the reversible cases it will suffice to show that the process and all its effects can be completely undone. In the irreversible ones it should be *assumed* that the process can be completely undone, and then a perpetual-motion machine of the second kind should be devised.

The Criterion of Irreversibility

In the preceding section a process was proved to be irreversible by, first, assuming it to be reversible, and, second, showing the assumption to be absurd by devising a perpetual-motion machine of the second kind that is made possible by it. Thus, the criterion of irreversibility may be stated as follows: *A process is irreversible if a perpetual-motion machine of the second kind would result from its being reversible.*

This criterion may be applied directly to many simple operations, of which those of the preceding section are examples. In other instances it becomes extremely cumbersome, and then it is better to employ the Inequality of Clausius or the Principle of the Increase of Entropy, both of which are formulations of the criterion of irreversibility.

The Reversible Process as a Limiting Process

Any process which involves the motion of a boundary of a system (the motion of a piston, for example) must be executed indefinitely slowly if it is to be reversible. For, if the fluid should be accelerated as the boundary moves, the force applied by it for inward motion would be greater than for the reverse motion, and more work would be taken from the environment during the inward motion than could be restored to it during the reverse motion.

Any process which involves a transfer of heat must also be executed indefinitely slowly if it is to be reversible. For if the system should be heated at a finite rate it must be lower in temperature than the source of heat by a finite amount in order to overcome resistance to the transfer of heat. It was shown above that no process which involves transfer of heat across a finite interval of temperature can be reversible.

Reversibility, then, demands not only that friction be absent and unrestrained expansions be avoided, but also that the process be executed with infinite slowness. It is so obvious that these conditions will not be encountered in our experience that we may state definitely that a reversible process can never be realized. On the other hand, the irreversible processes discussed above, which employed friction, transfer of heat across a finite interval of temperature, finite velocity of a piston, and unrestrained expansion, are common occurrences. For example, it is impossible to move a piston in a cylinder or even to move one part of a gaseous system relative to another part without setting up those shearing forces which are called friction. It is always possible by lubrication to reduce the friction of the piston in the cylinder; and it is always possible by reducing relative velocities to reduce the friction in a fluid mass. Generally, we may reduce friction as near to zero as we please, but for no finite motion executed in finite time will friction vanish. The frictionless process is thus a limiting one which actual processes may be made to approximate.

So it is with reversible processes in general. They are limiting cases of actual processes. By taking pains we may bring an actual process as near to reversibility as we please, but we cannot make it entirely reversible. Like the frictionless fluid of hydromechanics, the reversible process is a hypothetical device which plays an important part in scientific reasoning.*

Reversibility in Steady Flow

The definition of a reversible process given above applies to any system which takes part in steady flow through an apparatus: that is, a steady-flow process is reversible if an apparatus can be devised which will restore the stream to its initial state and leave no change in the environment. Thus, expansion of a fluid in steady flow through a frictionless nozzle (1 to 2, Fig. 33) may be reversible because a frictionless diffuser (3 to 4, Fig. 33) may cause the stream to leave in the same state (4) as that (1) in which it entered. Similarly the flow of steam

* It has been said that an irreversible process makes history. A reversible process can be completely undone, so that no trace — not even a fatigue — need remain. In this respect it is equivalent to the absence of a process.

through a frictionless turbine may be reversible, because the exhaust steam may be restored to its initial state in a compressor which will absorb precisely the amount of work delivered by the turbine and thus leave the environment unchanged.

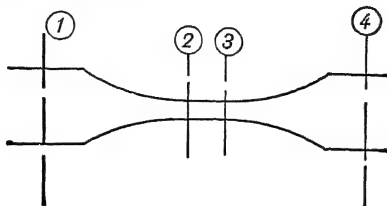


FIG. 33

In both the nozzle and the turbine the succession of states will be that of a reversible adiabatic process for which $du/dv = -p$ as explained on page 26.

PROBLEMS

1. Indicate whether the following processes are reversible or irreversible. In each reversible one justify your conclusion by showing that all effects of the process can be completely undone. (Neglect heat transfer unless the contrary is indicated.) In each irreversible one devise a perpetual-motion machine of the second kind which would be a consequence if the process were reversible.

(a) Gas is compressed slowly behind a leak-proof piston in a cylinder with non-conducting walls.

(b) The temperature of a mass of gas confined in a rigid container is raised by rotating a fan impeller inside the mass of gas.

(c) Some water confined under a piston of constant weight is stirred until half of it evaporates.

(d) Some water confined as in (c) is evaporated by a slow addition of heat.

(e) Gas is expanded slowly behind a leak-proof piston in a cylinder with conducting walls which are surrounded by a constant-temperature bath.

(f) Gas expands slowly through a small orifice from one chamber into an adjacent chamber where the pressure is markedly lower.

(g) A heavy piston confining a gas in a vertical cylinder is held in position by stops. When the stops are removed the piston falls because it has much more weight than the initial pressure of the gas can support.

(h) A weight slides frictionlessly down an inclined plane.

(i) A weight slides down a rough surface, being retarded by friction.

(j) A stream of fluid passes through ideally shaped fan blades without frictional resistance and without pressure drop. An observer standing on the fan blade sees no change in the stream speed between entrance and exit. A stationary observer sees a marked increase in stream speed between entrance and exit.

(k) The fluid stream leaving the fan in (j) is introduced into a large room where it eddies around until it leaves the room slowly through a large opening.

(l) Steam on its way to a steam turbine expands adiabatically through a reducing valve.

(m) Steam expands adiabatically in steady flow through a frictionless nozzle.

(n) An iron ball is cooled from a temperature of 100 F to 70 F by submersion in a large body of water.

(o) A cylinder contains a leak-proof piston and two masses of air separated by the piston. The piston is moved suddenly through an appreciable distance to the right, causing the pressure and temperature of the air on the right to rise and causing a reverse effect on the air on the left. By virtue of the temperature difference a flow of heat occurs which restores temperature equilibrium between the two air masses.

(p) A stream of water is raised in temperature from 60 F to 200 F by mixing it with a stream of steam at 212 F.

SYMBOLS

p	pressure
u	internal energy of a unit system in the absence of motion, gravity, etc.
v	specific volume

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CHAPTER VIII

COROLLARIES OF THE SECOND LAW

Corollary 1

It is impossible to construct an engine to work between two heat reservoirs, each having a fixed and uniform temperature, which will exceed in efficiency a reversible engine working between the same reservoirs.

PROOF: Assume that an engine I can be constructed which will exceed in efficiency a reversible engine R working between the same two reservoirs (Fig. 34).

Let W_I denote the work done by engine I when it receives heat q_1 , and let W_R denote the work done by engine R when it receives the same amount of heat. Then, by assumption, we get

$$W_I > W_R.$$

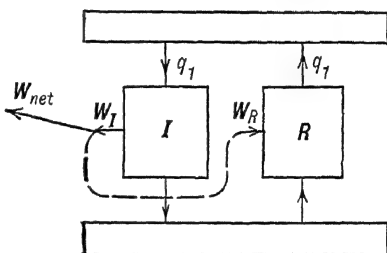


FIG. 34

Now let engine R be reversed so that it will supply to the high-temperature reservoir the heat q_1 while engine I takes from it the same amount of heat. Since a conductor between R and I could be substituted for the reservoir, and since the work delivered by I would exceed the work received by R , the combination constitutes a perpetual-motion machine of the second kind. In view of the Second Law, therefore, Corollary 1 must be true.

Corollary 2

All reversible engines have the same efficiency when working between the same two reservoirs.

The proof of Corollary 2 is like the proof of Corollary 1; it is assumed that the opposite is true in a single instance and it is shown that the Second Law would be violated as a consequence.

Corollary 3

A temperature scale may be defined which is independent of the nature of the thermometric substance.

It was pointed out on p. 4 that if two isolated systems are at different levels of temperature the difference is made evident when a body

from one system is brought in contact with a body from the other system by a change in the properties of both the bodies. The magnitude of any property which changes with temperature can be used as a measure of temperature, and a temperature scale can be defined in terms of it. The body is then called a thermometer.

If a thermometer is to be used under a variety of circumstances it is necessary that the body which constitutes it should be restrained in some prescribed way under all circumstances, or the same value of the thermometric property might not always indicate the same level of temperature. For instance, a given mass of mercury at the temperature of melting ice will not fill the same volume under a pressure of 1 atmosphere as under a pressure of 1000 atmospheres. But if the mercury in the thermometer is kept always under a pressure of 1 atmosphere, even when it is used to measure the temperature of a fluid which is under a pressure of 1000 atmospheres, then the volume of the mercury is a satisfactory indicator of temperature.

Temperature scales have been defined in terms of many different properties of many different substances; the following are a few examples:

The volume of a liquid at atmospheric pressure.

The volume of a liquid confined in a closed tube by a gas.

The volume of a fixed mass of gas at constant pressure.

The pressure of a fixed mass of gas at constant volume (or in a given container).

The length of a metal rod at atmospheric pressure.

The electrical resistance of a metal wire at atmospheric pressure.*

The color of a piece of metal.

The emf of a pair of metals with one metallic junction at a reference temperature and a second at the temperature to be measured.

Though the number of possible temperature scales included in the eight classifications listed is indefinitely large, each scale differs from all the others. The values of the ice point and the boiling point of water may be fixed by definition so that they are the same on every scale, but at all other levels of temperature the various scales will depart from each other in varying degrees. The Second Law, on the other hand, permits the definition of a temperature scale which is independent of the nature of the thermometric substance.

PROOF: Consider reversible engines 12, 23, and 13 working respec-

* Bridgman has shown that electrical resistance varies with pressure on the wire as well as with temperature. *The Physics of High Pressure*, Bridgman, Macmillan Co., pp. 257-294.

tively between reservoirs at temperature levels t_1 and t_2 , t_2 and t_3 , and t_1 and t_3 (Fig. 35). Let engine 12 receive heat q_1 at temperature t_1 and reject heat q_2 at temperature t_2 ; let engine 23 receive heat q_2 at temperature t_2 and reject heat q_3 at temperature t_3 ; let engine 13 receive heat q_1 at temperature t_1 and reject heat q_3 at temperature t_3 .

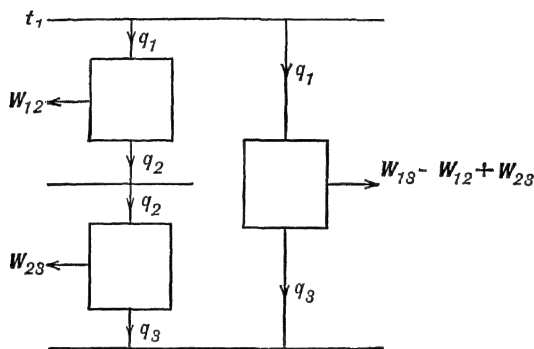


FIG. 35

The efficiency of engine 12 is fixed, according to Corollary 2, by the temperatures of reservoirs 1 and 2. Therefore, if we choose any one scale of temperatures and denote the temperatures of the three reservoirs on this scale by t_1 , t_2 , and t_3 , we may write

$$\eta_{12} = f(t_1, t_2)$$

where η_{12} denotes the efficiency of engine 12 and f denotes a functional relationship whose form is determined by the nature of the scale of temperature. Since the efficiency may also be expressed in the form

$$\eta_{12} = 1 - \frac{q_2}{q_1},$$

it is permissible to write

$$\frac{q_1}{q_2} = \phi(t_1, t_2),$$

where ϕ denotes another functional relationship. We may also write

$$\frac{q_2}{q_3} = \phi(t_2, t_3)$$

and

$$\frac{q_1}{q_3} = \phi(t_1, t_3).$$

Since engines 12 and 23 in combination constitute a reversible engine working between reservoirs 1 and 3, the efficiency of the combination

must, by Corollary 2, be identical with the efficiency of engine 13. Therefore, q_3 and q_3' are equal and the last equation becomes

$$\frac{q_1}{q_3} = \phi(t_1, t_3).$$

The three heat ratios stated above are related by the equation

$$\frac{q_1}{q_2} = \frac{q_1/q_3}{q_2/q_3},$$

which becomes upon substitution of the function ϕ

$$\phi(t_1, t_2) = \frac{\phi(t_1, t_3)}{\phi(t_2, t_3)}.$$

Therefore, t_3 , which is arbitrary, must cancel from the right-hand member, leaving an equation of the form

$$\phi(t_1, t_2) = \frac{\psi(t_1)}{\psi(t_2)}$$

or

$$\frac{q_1}{q_2} = \frac{\psi(t_1)}{\psi(t_2)}, \quad [10]$$

where ψ denotes another unknown function. The form of this function is determined by the nature of the chosen scale of temperature and may therefore be one of an infinite variety of possible forms. If a single form is selected, a scale of temperature is thereby defined which is independent in its definition of any thermometer other than the reversible engine implied by [10]. Such a scale would be called a *thermodynamic temperature scale*. It would be entirely independent of the thermometric substance — that is, the material used in the reversible engine — because the efficiency of a reversible engine, and, therefore, the ratio of its quantities of heat, is independent of the nature of the engine.

The Kelvin Temperature Scale

Temperature on the *Kelvin scale*, which we shall denote by T , is given by the relation

$$\psi(t) = T,$$

or, alternatively, by

$$\frac{q_1}{q_2} = \frac{T_1}{T_2}. \quad [11]$$

The size of the degree or unit of temperature is established by fixing at 100 degrees the interval of temperature between melting ice and con-

densing water vapor, both under a pressure of 1 standard atmosphere.*

The Kelvin scale is also called the *absolute Centigrade scale*. Another scale which is defined by [11] subdivides the interval between melting ice and boiling water into 180 degrees. It is known as the *absolute Fahrenheit scale*. In subsequent pages the symbol T will be used to denote a temperature on either of these scales.

Two other thermodynamic scales of temperature are defined in terms of these absolute scales so as to resemble the old mercury-in-glass scales. They are the *thermodynamic Centigrade scale* on which the temperature is less than the Kelvin scale temperature by the temperature of the ice point on the Kelvin scale, and the *thermodynamic Fahrenheit scale* on which the temperature is less than the absolute Fahrenheit temperature by the temperature of the ice point on that scale reduced by 32. In subsequent pages the symbol t will be used to denote a temperature on either the Centigrade or the Fahrenheit thermodynamic scale.

It is difficult, though entirely possible, to determine temperatures on the absolute scale. For most practical purposes we must be content with approximations. However, in the usual range of engineering experience the absolute temperatures corresponding to certain reproducible levels of temperature are known with good precision. For example, the temperature of the ice point is known within a few hundredths of a degree Kelvin, and the temperature of the boiling point of sulphur within about one-tenth of a degree.

The following table compares values on the four scales defined above:

TEMPERATURE LEVEL	CENTIGRADE	CENTIGRADE	FAHRENHEIT	FAHRENHEIT
Absolute zero	0	-273.16	0	-459.69
Ice point	273.16	0	491.69	32
Condensation or				
boiling point of water	373.16	100	671.69	212
Boiling point of sulphur	717.8	444.6	1292.0	832.3

Absolute Zero of Temperature

Corollary 3 has two subcorollaries as follows:

3a. It is impossible to attain negative temperatures on the absolute scale.

3b. It is impossible (in the absence of a perfect heat insulator) for a finite system to attain zero temperature on the absolute scale.

* A standard atmosphere is the pressure due to a column of mercury, at the temperature of melting ice, 760 mm in height under an acceleration of gravity of 980.665 cm/sec². Corresponding conversion formulas are

$$\begin{aligned} 1 \text{ standard atmosphere} &= 14.696 \text{ lb/sq in.} \\ &= 1.03323 \text{ kg/sq cm.} \end{aligned}$$

To prove Corollary 3a it is only necessary to note that the usual heat rejection from a reversible engine would become a heat supply at negative temperatures. Both the high-temperature heat supply and the low-temperature one could be provided from a single reservoir whose temperature was sufficiently high. The engine would, therefore, constitute a perpetual-motion machine of the second kind. This, by the Second Law, is impossible.

To prove Corollary 3b it should be noted that any flow of heat from the environment to a system at absolute zero of temperature could be pumped out of the system only at the expense of an amount of work which is infinitely great compared with the heat. In the absence of a perfect insulator, the heat would be finite — the work required would, therefore, be infinite.*

Efficiency of a Reversible Engine

The definition of the efficiency of a heat engine is given by the equation

$$\eta = \frac{W}{q_1},$$

where W denotes the net work delivered by the engine during an integral number of cycles and q_1 the corresponding quantity of heat received

* Before the introduction of the present thermodynamic scale of temperature Kelvin suggested a scale which had numbers ranging from $-\infty$ to $+\infty$, all within the possible range of temperatures which is covered by numbers ranging from 0 to $+\infty$ in the present scale. It was defined by the relation

$$\frac{q_1}{q_2} = \frac{\ln^{-1} \theta_1}{\ln^{-1} \theta_2},$$

where q_1 and q_2 denote the heat received and rejected, respectively, by a reversible engine, and θ_1 and θ_2 the temperatures of heat reception and rejection, respectively, on Kelvin's first scale. It is easy to show that the first scale is related to the present scale as follows:

$$\theta_1 - \theta_2 = \ln T_1 - \ln T_2,$$

and, therefore,

$$\theta = \ln T + C,$$

where C is an arbitrary constant the magnitude of which determines what level of temperature will correspond to zero on the scale of θ .

The efficiency of a reversible engine between temperatures t and $t - \delta t$, when δt is infinitesimal, may be used to define a quantity μ through the equation

$$\eta = \mu \delta t.$$

The quantity μ , which is known as *Carnot's function*, can be shown to be $1/T$ for the present Kelvin scale. Kelvin arrived at his first scale by making μ equal to unity. It was found, then, that the coefficient of thermal expansion of a perfect gas at constant pressure — $(1/v)(\partial v / \partial \theta)_p$ — is also unity in terms of the first scale.

from the source. From this definition and the First Law [1a] we get

$$\eta = \frac{q_1 - q_2}{q_1}$$

which in combination with the definition of the absolute scale of temperature [11] gives

$$\eta = \frac{T_1 - T_2}{T_1} \quad [12]$$

where subscripts 1 and 2 refer respectively to heat source and heat sink. The last equation [12] holds for any reversible engine which receives heat at temperature T_1 , rejects heat at temperature T_2 , and experiences no other exchange of heat with its environment.

Corollary 4 — The Inequality of Clausius

Whenever a system executes a complete cyclic process, the integral of dQ/T around the cycle is less than zero, or in the limit is equal to zero.

PROOF:* Consider a system which executes a cyclic process while work and heat cross its boundaries. For purposes of analysis, let each element of heat dQ that is received by a part of the system at temperature T be supplied reversibly from a constant-temperature reservoir through a reversible engine (R , Fig. 36). We may, of course, consider the reversible engine to be minute, so that for each transfer of heat to the system of magnitude dQ the engine executes one or more complete cycles. Let dW denote the work delivered by the reversible engine while the system receives heat dQ , and let dw denote the work delivered during the same interval by the system to its environment. Any of the three quantities dQ , dW , and dw may assume negative values as well as positive values, the difference between the two corresponding, as usual, to a difference in the direction in which heat or work crosses the boundary.

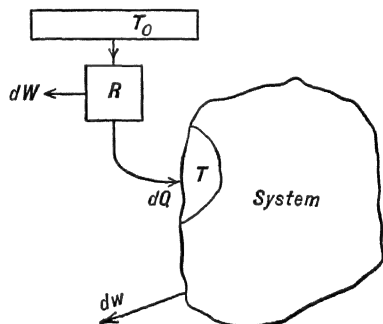


FIG. 36

Applying the First Law [1a] to the cycle executed by the system, we get

$$\oint dw = \oint dQ.$$

* The proofs of Corollaries 4, 5, and 6 are paraphrases of some unpublished notes on the Second Law of Thermodynamics by H. B. Phillips.

The heat transferred to the system at various temperatures T may come from the reservoir, whose temperature is T_0 , through a multiplicity of reversible engines like R , each of which executes an integral number of complete cycles while the system executes one cycle. From the definition of the temperature scale [11] we get the following relation between dW and dQ :

$$\frac{dW + dQ}{dQ} = \frac{T_0}{T},$$

or

$$dW = \left(\frac{T_0}{T} - 1 \right) dQ.$$

The total work of the combined system and reversible engine is given by

$$\sum \text{work} = \oint dw + \oint dW,$$

which by substitution from above becomes

$$\sum \text{work} = \oint dQ + \oint \left(\frac{T_0}{T} - 1 \right) dQ = T_0 \oint \frac{dQ}{T}.$$

The combined system and reversible engine constitute a perpetual-motion machine of the second kind if the total work ($\sum \text{work}$) is greater than zero. Therefore, upon noting that T_0 is greater than zero, we may write

$$\frac{dQ}{T} \leq 0.$$

This result is known as the *Inequality of Clausius*.

Corollary 5

The cyclic integral of dQ/T is equal to zero for any reversible cyclic process; and, consequently, the integral of dQ/T for any reversible process between a reference state 0 and any other state 1 is a property of the system in state 1.

Let us consider a system S' (Fig. 37) which executes a reversible cyclic process. A certain group of things external to the system S' are affected during this process by work and heat that pass to and from S' . Let us consider this external group of things to be a second system S'' . Since nothing is affected except S' and S'' all heat must flow from one of these systems to the other; therefore, we may write

$$dQ' = -dQ'',$$

where dQ' denotes heat flowing to S' if it is positive and heat flowing from S' if it is negative, and dQ'' denotes the same as regards S'' .

If heat flows from S'' to S' , then the temperature from which it flows, T'' , must be greater than that to which it flows, T' . Moreover, dQ' denotes a positive number and, by $[a]$, $-dQ''$ denotes the same number. Therefore, we get

$$\frac{dQ'}{T'} > -\frac{dQ''}{T''} \quad [b]$$

It can as readily be shown that this inequality holds as well for heat flow in the other direction.

Now let S' execute a reversible cyclic process. By the definition of a reversible process, everything external to S' , that is, everything affected by the process, may be returned to its initial state after the process has occurred. Thus, S'' may also execute a cycle. Upon integrating $[b]$ over the two cyclic processes, we get

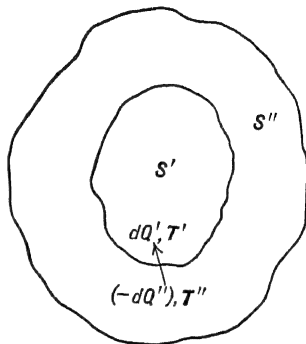


FIG. 37

$$\oint \frac{dQ'}{T'} \geq -\oint \frac{dQ''}{T''},$$

or

$$\frac{dQ'}{T'} + \frac{dQ''}{T''} \geq 0. \quad [c]$$

The Inequality of Clausius holds for any cycle, reversible or irreversible, and we may therefore write

$$\oint \frac{dQ'}{T'} \leq 0,$$

and

$$\oint \frac{dQ''}{T''} \leq 0. \quad [d]$$

The only way in which both $[c]$ and $[d]$ can be satisfied is to have the cyclic integrals for both systems equal to zero:

$$\oint \frac{dQ'}{T'} = 0 = \oint \frac{dQ''}{T''}.$$

It follows that for any reversible cyclic process the integral of dQ/T is zero; that is

$$\oint_{\text{rev}} \frac{dQ}{T} = 0. \quad [13]$$

The following is a less general and less rigorous proof that is commonly employed because it is graphic:

Let a cyclic process which can be executed reversibly be represented by the closed curve C in Fig. 38. Let the area within C be cut into a large number of strips by reversible adiabatic lines 11, 22, etc. Where each reversible adiabatic line intersects the curve C , let an isothermal line be drawn to the right until it meets the adjacent reversible adiabatic line. Now each pair of reversible adiabatics together with the isothermals joining them constitute a Carnot cycle.

According to the definition of temperature we may write for any Carnot cycle

$$\frac{q_1}{T_1} = \frac{q_2}{T_2},$$

where q_1 and q_2 denote respectively heat received and rejected by the system and T_1 and T_2 denote the temperatures of the source and sink. Using the symbol Q in the general sense of heat flowing to the system (so that $q_2 = -Q_2$), we have

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0.$$

If the closed path C is approximated by the stepped path 1a2b, etc., made up of the ends of the Carnot cycles, then we may write for the circuit

$$\sum \frac{Q}{T} = 0.$$

For, each step involves a value of Q/T along the isothermal which is exactly canceled by the opposite isothermal in the same Carnot cycle, and no heat is transferred in the adiabatic steps. Now, if the number of Carnot cycles within C is increased indefinitely the stepped path can be made to approach path C as nearly as we please, and

$\sum Q/T$ becomes $\oint dQ/T$. Therefore, we get

$$\oint \frac{dQ}{T} = 0.$$

To make this proof rigorous it would be necessary, first, to show that any reversible cycle can be subdivided into elementary Carnot cycles, and, second, that the limit of the integral of dQ/T for the stepped path is identical with the integral for the actual path.

Let path A in Fig. 39 represent a reversible process proceeding from state 1 to state 0; and let paths B and C represent any two different reversible processes proceeding from state 0 to state 1. Then according to [13] we may write

$$\int_{1A}^0 \frac{dQ}{T} + \int_{0B}^1 \frac{dQ}{T} = 0,$$

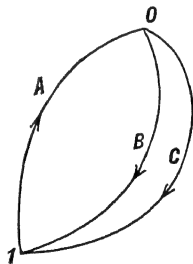


FIG. 39

and

$$\int_{1A}^0 \frac{dQ}{T} + \int_{0C}^1 \frac{dQ}{T} = 0.$$

Subtracting and transposing, we get

$$\int_{0B}^1 \frac{dQ}{T} = \int_{0C}^1 \frac{dQ}{T}.$$

Therefore, the integral of dQ/T computed for any reversible process between the reference state 0 and any other state 1 is independent of the process and is, consequently, a property of the system in state 1.

This property is called the *entropy* of a system. It is represented by the symbol S for a system as a whole or by s for unit mass of a system. Thus,

$$dS = \left(\frac{dQ}{T} \right)_{\text{rev.}} \quad \text{and} \quad S_2 - S_1 = \int_{1 \text{ rev.}}^2 \frac{dQ}{T}. \quad [14]$$

Entropy and the Second Law

As a consequence of the First Law a property called *internal energy* is discovered; as a consequence of the Second Law a property called *entropy* is discovered. There is, however, a difference in nature between these two quantities that may well be borne in mind: the change in internal energy may be evaluated from work and heat in any process joining two states, provided only that work and heat can be identified in the process; but the change in entropy can be evaluated from heat and temperature only in a *reversible* process joining two states. Since entropy is a property, the change in its value between two states is independent of the process joining them, but *only in a reversible process will it be identical with the integral of dQ/T* . It is proved below that for all other processes the change in entropy is greater than the integral of dQ/T .

Use of Entropy

The property entropy will be used frequently in subsequent pages, but to justify its introduction a few examples of its usefulness will be given here.

For any process joining two states on any *reversible adiabatic* path which a system may follow we may write

$$\Delta S = \int_{\text{rev.}} \frac{dQ}{T} = 0.$$

We shall employ this relationship to trace on a diagram of properties a reversible adiabatic path for a pure substance uninfluenced by gravity, electricity, magnetism, or capillarity:

Starting from the initial state A on the u - v diagram (Fig. 40) let a unit mass of the substance change at constant volume to another state B' . From A to B' the change in entropy is

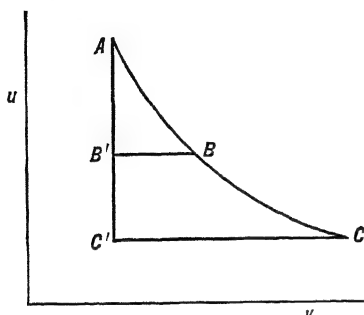


FIG. 40

$$\Delta s = \int_{A \text{ rev.}}^{B'} \frac{dQ}{T} = \int_A^{B'} \frac{du}{T}$$

according to [2]. Next let it change reversibly at constant internal energy from B' toward B . This change may be accomplished according to [2] by confining the substance in a cylinder behind a piston and allowing the piston to move out slowly while heat is added at precisely the rate at which work

is done on the piston. The work on the piston for each increment of volume dv is $p dv$, so that the change in entropy becomes

$$\Delta s = \int_{\text{rev.}} \frac{dQ}{T} = \int \frac{p dv}{T}.$$

A few trials will find a point B corresponding to which

$$\Delta s \Big|_A^B = \int_A^{B'} \frac{du}{T} + \int_{B'}^B \frac{p}{T} dv = 0.$$

The point B is, therefore, a second point on the reversible adiabatic path which passes through A . Similar calculation along the lines AC' and $C'C$ will locate a third point C , and so forth, until enough points are found to determine the reversible adiabatic path completely.

This method is much easier than the one described on page 26, because the path to be integrated can be chosen beforehand and the integration can be carried out in a familiar fashion. The property entropy makes the simpler method possible.

The heat transferred, Q_T , to a system during a *reversible isothermal process* at temperature T between states 1 and 2 may be expressed in the form

$$Q_T = T(S_2 - S_1),$$

according to the definition of entropy. Without the entropy, on the other hand, it can be calculated from [2] which for a *reversible process executed by unit mass of a pure substance* is

$$dQ = du + p dv$$

or
$$Q_T = u_2 - u_1 + \int_1^2 p \, dv.$$

To evaluate the first expression for Q_T only the end states need be known, but to evaluate the second a knowledge of all intermediate states is necessary.

Calculation of Entropy Changes for a Pure Fluid Substance

Any valid method of calculating the change in entropy of a system can be justified from the definition

$$\Delta S = \int_{\text{rev.}} \frac{dQ}{T}.$$

According to [2] the definition of entropy may be written in the form

$$dS = \left(\frac{dE + dW}{T} \right)_{\text{rev.}}$$

The work in each step of the reversible change must not involve friction forces; that is, the paddle-wheel type of work must be excluded. The only kind of work permitted in the absence of motion, gravity, electricity, magnetism, and capillarity is work done by normal forces (not shearing forces) at slowly moving boundaries of the system. Therefore, we may write for a homogeneous system of unit mass

$$dW_{\text{rev.}} = p \, dv.$$

Moreover, within these same restrictions the internal energy is a function of two independent properties, so that it may be denoted by u for a homogeneous system of unit mass. The expression for change in entropy becomes, in consequence,

$$ds = \frac{du + p \, dv}{T}. \quad [15]$$

If the relationship between p , v , T , and u is known for a given pure substance the change in entropy between any two states may be computed from [15] without measuring heat and work.* The computed values must be the same for all paths between the same two states. The agreement between the values for different paths may be used as a test of the validity, in view of the First and Second Laws, of the relationship between p , v , T , and u .

* Of course, the p - v - u relation can be known only if measurements of heat and work have been made previously.

The Temperature-Entropy Diagram and Other Diagrams of Properties

Entropy like any other property may be used as a coordinate in a diagram of properties. From its definition [14], which may be written $T ds = dQ_{\text{rev.}}$, we find that the area under a path on the temperature-

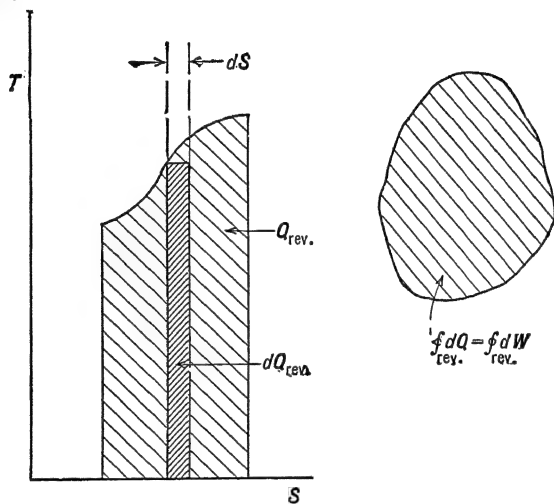


FIG. 41

entropy diagram represents the heat received by the system when that path is followed reversibly (Fig. 41). Similarly the area within any closed path represents the net heat received by the system when the system passes reversibly through the corresponding cycle. According to the First Law [1a], the same enclosed area is equal to the net work delivered by the system when the system passes reversibly through the cycle. Thus

$$\oint T ds = \oint_{\text{rev.}} dQ = \oint_{\text{rev.}} dW.$$

The temperature-entropy diagram for liquid and vapor water is shown in Fig. 42. If some liquid initially in state L' is heated reversibly at constant pressure until it reaches the saturated liquid state L , the heat added is shown by the area under the line of constant pressure $L'L$. The heat added during reversible vaporization is shown by the rectangular area under the isotherm LV . Similarly, the heat added during reversible superheating of the vapor is shown by the area under the line VV' . The line of constant entropy $V'V''$ has no area beneath it and therefore represents a reversible adiabatic change.

Any of these lines may represent the paths of irreversible processes. but then the areas under the curves would not represent the heat of the

processes. For example, an irreversible process along the path $V'V''$ is not adiabatic. Again, a fluid in steady flow through a porous plug changes along a line of constant enthalpy from high pressure to low, $P'P''$. The area under the curve is finite but the process is adiabatic. Note, however, that the entropy increases during the process.

Besides the temperature-entropy diagram the pressure-volume and enthalpy-entropy diagrams are commonly used to show the properties of a substance. The first two are used primarily for purposes of illustration and demonstration, because the area under a curve on the pressure-volume chart represents the work done by a pure substance in a simple reversible process, and the area under a curve on the temperature-entropy chart represents the heat received under the same conditions. An example of a temperature-entropy diagram is shown in Fig. 1. Keenan and Keyes.

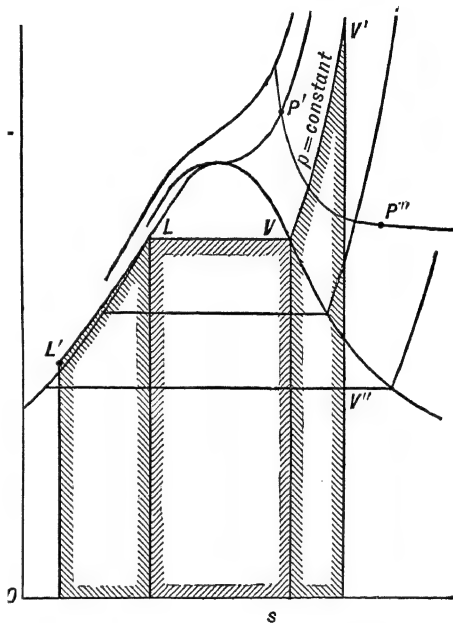


FIG. 42. Temperature-Entropy Chart for Water

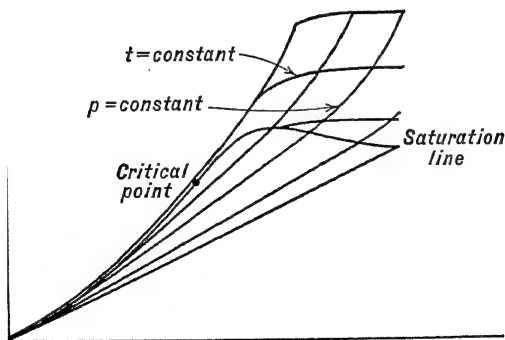


FIG. 43. Mollier Chart for Water

The frequent occurrence of the reversible adiabatic process in engineering analysis prompts the adoption of entropy for one of the coordinates of a working chart, whereas the importance of the steady-flow process suggests enthalpy for the other. The enthalpy-entropy chart is probably the chart most commonly employed as an aid in engineering calculations. It is called the Mollier chart in honor of Richard Mollier, who first proposed its adoption. A small-scale Mollier chart is shown in Fig. 43. One of sufficiently large scale for engineering use accompanies the *Tables* of Keenan and Keyes.

Corollary 6 — Principle of the Increase of Entropy

The entropy of an isolated system increases or in the limit remains constant.

PROOF: Let a system change from state 1 to state 0 (Fig. 44) by a reversible process and return from state 0 to state 1 by either of two possible processes, one reversible and one irreversible. Using subscript *R* to indicate a reversible process and *I* to indicate an irreversible process we may write by Corollary 4

$$\frac{dQ}{T} + \int_{0I}^1 \frac{dQ}{T} \leq 0,$$

and by Corollary 5

$$\int_{1R}^0 \frac{dQ}{T} + \int_{0R}^1 \frac{dQ}{T} = 0.$$

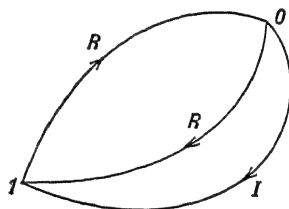


FIG. 44

Subtracting the second from the first, we get

$$\int_{0I}^1 \frac{dQ}{T} - \int_{0R}^1 \frac{dQ}{T} \leq 0.$$

Differentiating, substituting dS for $(dQ/T)_R$, and transposing, we get

$$dS \geq \frac{dQ}{T}. \quad [16]$$

For an isolated system dQ must be zero, and therefore

$$dS_{\text{isol}} \geq 0. \quad [17]$$

This is the celebrated *principle of the increase of entropy*. Though it refers to an isolated system, it is nevertheless of extremely general application, for all material that is in any way affected by a process may be included within a single isolated system.

Let us consider a few simple examples of the application of the principle of the increase of entropy. If a marble is rolling about inside a non-conducting sphere, we know from experience that, barring disturbances, the marble will ultimately come to rest at the bottom of the sphere. The final state of the system comprising marble and sphere must be one of higher entropy. Again, if a cube of copper receives heat from a surrounding water bath and nothing else is affected, the final state of the copper-water system must be one of higher entropy. The increase in the entropy of the copper must have exceeded the decrease in the entropy of the water—a conclusion easy to verify from the definition of entropy. Even more complicated examples may be given. Suppose, for instance, that a minute spark ignites a combustible mixture of gasoline and air in the cylinder of an automobile engine. A chemical reaction may result so suddenly that transfer of heat to the surrounding walls during the reaction is vanishingly small. Then the state of the system as products of combustion is one of higher entropy than the initial state.

The principle of the increase of entropy is in itself a *criterion of irreversibility*. It states that the entropy of an isolated system must either increase or remain unchanged. Since entropy is defined by the relation

$$dS = \left(\frac{\delta Q}{T} \right)_{\text{rev.}}, \quad [14]$$

for any reversible process the entropy of an isolated system remains unchanged. Therefore, we may say that *if the entropy of an isolated system increases during a process then the process is irreversible*. This criterion is, in fact, identical with the one stated on page 69, because, if we could undo a process in an isolated system which had caused an increase in entropy, then it would be possible to devise a perpetual-motion machine of the second kind.

Corollary 2 of the First Law states that, if an isolated system has at any instant a given internal energy, it can assume later only those states which have the same internal energy, regardless of the processes that ensue. Corollary 6 of the Second Law restricts still further the possible subsequent states. Of the states of equal internal energy, only those of higher entropy than the initial state can be assumed by the system.* Furthermore, if the initial state is higher in entropy than all

* Clausius stated these two corollaries in cosmic form: namely, "The energy of the universe is constant; the entropy of the universe increases toward a maximum." Even for a science as general as thermodynamics these phrases are a bit presumptuous. Moreover, they cannot serve as a basis for conclusions concerning finite systems.

other states having the same internal energy, then no change can ensue. The system is then said to be in stable equilibrium. This is the basis of Chapter XXVI, which deals with equilibrium.

PROBLEMS

1. The second law of thermodynamics is stated in one textbook as follows: "It is impossible for a self-acting machine unaided by any external agency to convey heat from one body to another at higher temperature."

(a) Devise a machine which includes an ordinary refrigerator which would violate the law thus stated.

(b) How would you modify this statement to make it true?

(c) Prove that your modified statement is true starting from the statement of the Second Law given on page 64.

2. Starting from the Second Law as stated on page 64 prove Corollary 2 of page 73.

3. A reversible engine receives 100 Btu of heat from a large high-temperature source, delivers 20 kw-sec of work, and rejects heat to a large low-temperature sink. Find:

(a) The ratio of the Kelvin scale temperatures of the source and sink.

(b) The ratio of the absolute Fahrenheit temperatures of source and sink.

(c) The temperature of the source on the Centigrade scale if the temperature of the sink is 400 F abs.

(d) The temperature of the source on the Fahrenheit scale if the temperature of the sink is 200 K.

4. A reversible engine receives its heat from a mixture of water vapor and liquid water under a pressure of 1 atmosphere and rejects 3600 Btu/hr of heat to a mixture of ice and liquid water under a pressure of 1 atmosphere. It delivers 0.386 kw power. From these data find the number of degrees separating absolute zero and the ice point on the Kelvin scale.

5. In the cycles described on pages 8 and 9, find the values of $\oint ds$ and $\oint dQ/T$ relative to zero:

(a) for the cycle in which $\oint dW = 0$.

(b) for the cycle in which $\oint dW \neq 0$.

6. In a certain *reversible* cycle 100 Btu of heat is received at a temperature of 500 K; then an adiabatic expansion occurs to 400 K, at which temperature 50 Btu of heat is received; then a further adiabatic expansion to 300 K, after which 100 Btu of heat is rejected at constant temperature.

(a) Find the change in entropy which occurs as the system is restored to its initial state in the remainder of the cycle.

(b) If during the remainder of the cycle heat is transferred only at 400 K, how much heat is transferred, and in which direction?

7. (a) In a certain reversible process the rate of heat transfer to the system per unit temperature rise is constant and is given by

$$\frac{dQ}{dT} = 0.5 \text{ Btu/F}$$

Find the increase in entropy of the system if its temperature rises from 500 F abs to 600 F abs.

(b) In a second process between the same end states the temperature rise is accomplished by stirring accompanied by a heat addition half as great as in (a).

What is the increase in entropy in this case?

8. Find first from the First Law and second using the entropy, the heat transferred to a pound of steam in the following *reversible* processes:

(a) Evaporation of saturated liquid to saturated vapor at 212 F.

(b) Constant-temperature expansion of superheated steam from 500 F, 250 lb/sq in. abs to 100 lb/sq in. abs.

(c) Constant-volume heating from saturated vapor at 50 lb/sq in. abs to 100 lb/sq in. abs.

9. Find the work done *on a piston* per pound of water in the following reversible adiabatic processes:

(a) Expansion from 500 F, 250 lb/sq in. abs to 150 lb/sq in. abs.

(b) Compression from saturated vapor at 15 lb/sq in. abs to 100 lb/sq in. abs.

(c) Expansion from saturated vapor at 15 lb/sq in. abs to 1 in. Hg abs.

(d) Compression from 875 lb/sq in. abs, 400 F, to 5500 lb/sq in. abs.

10. (a) Find the kinetic energy leaving a frictionless nozzle with non-conducting walls if the condition of the steam before the nozzle is 500 F, 250 lb/sq in. abs, its velocity is 200 ft/sec, and its final pressure is 150 lb/sq in. abs.

(b) Find the kinetic energy leaving a frictionless non-conducting diffuser passage at 350 lb/sq in. abs if the condition of the steam before the diffuser is 500 F, 250 lb/sq in. abs, and 2000 ft/sec velocity.

11. A Carnot reciprocating steam engine receives heat as water is evaporated from saturated liquid at 300 F to saturated vapor at the same temperature, and rejects heat at 100 F.

(a) Plot this cycle on a p - v diagram and on a T - s diagram.

(b) From the First Law equation compute the heat transferred in each part of the cycle.

(c) Compute the work done in each part of the cycle.

(d) How does the net work compare with the net heat transfer for the entire cycle?

(e) What is the thermal efficiency of the cycle? Does it agree with the definition of the thermodynamic temperature scale?

12. (a) Plot on a p - v diagram and on a T - s diagram a Carnot cycle for steam which extends between 500 F and 320 F and between extreme volumes of 2.722 cu ft/lb and 20 cu ft/lb.

(b) Find by the easiest method you know the net work done by each pound of steam in one cycle of operations.

13. Find in terms of properties the simplest expressions for infinitesimal and finite changes in entropy in the absence of motion, gravity, electricity, etc. during processes in which p , v , T , u , h , and (p and T) are respectively held constant.

14. In a certain imaginary *frictionless* turbine heat is added to the steam flowing through it so that the temperature of the steam is 500 F between the point where it enters at a pressure of 200 lb/sq in. abs and the point where it leaves at a pressure of 15 lb/sq in. abs. Neglect kinetic energies at entrance and exit. Notice that the expansion is reversible.

How much work is delivered to the turbine shaft per pound of steam entering the turbine?

15. Show that the increase in kinetic energy of each pound of fluid passing through a frictionless non-conducting nozzle passage is equal to $-\int v dp$.

16. (a) Find the inlet and outlet areas of the nozzle described in problem 10(a) if the flow through the nozzle for the conditions given is 10,000 lb/hr.

(b) For the same inlet conditions and the same flow as in (a) find the cross-sectional area of the stream where the pressure is 200, 140, 135, 130, 120, 100, 50, 10, and 1 lb/sq in. abs.

(c) Plot the area against the ratio of the pressure to the initial pressure. What is the minimum area (the throat area)?

17. Find the throat area, the exit area, and the area ratio for a frictionless nozzle which is to receive 5000 lb of steam per hour at 100 lb/sq in. abs, 500 F, and discharge it at 20 lb/sq in. abs. The inlet velocity is negligible.

18. Steam superheated 50 F at an initial pressure of 100 lb/sq in. abs expands through a non-conducting nozzle without friction and leaves with an exit velocity of 2238 ft/sec.

(a) What is the exit pressure if the inlet velocity is negligible?

(b) Assuming a throat area of 1 sq in., determine the weight of steam flowing per second and the exit area.

19. Steam at 150 lb/sq in. abs and 450 F expands through a non-conducting frictionless nozzle to a pressure of 10 lb/sq in. abs. The exit area is 1 sq in.

(a) If the initial velocity is zero, how much steam will pass through the nozzle per second?

(b) If the initial velocity is 500 ft/sec, what is the exit velocity?

20. A system consists of a marble in a bowl. The temperature of the system may be increased uniformly and reversibly by a slow addition of heat. For each Fahrenheit degree 1 Btu of heat must be added.

(a) Find the increase in entropy corresponding to a heat flow to the system of 1 ft-lb if the initial temperature of the system is 500 F abs.

If the marble is released at a vertical height of 4 ft above the bottom of the bowl and allowed to roll down the side it will oscillate for a while and then come to rest at the bottom of the bowl. The temperature of the system will ultimately be uniform.

(b) Find the increase in entropy of the system for an adiabatic process of this latter type if the initial temperature is 500 F abs and the weight of the marble is 0.25 lb.

21. A certain gas has a specific heat at constant volume of 0.3 Btu/lb F. When it is expanded reversibly and adiabatically from a specific volume of 1 ft³/lb and a temperature of 1000 F abs to a specific volume of 3 ft³/lb its temperature falls 300 F. When it is expanded adiabatically from the same initial state into an evacuated space to the same final specific volume its temperature falls only 50 F.

Find the magnitude of the change in entropy of one pound of gas in each of these adiabatic processes.

SYMBOLS

E	internal energy of a system in general
p	pressure
q	a positive number representing a quantity of heat
Q	heat to system
s	entropy per unit mass
S	entropy for system as a whole
t	temperature on any scale, temperature on Centigrade or Fahrenheit scales
T	temperature on Kelvin or absolute Fahrenheit scales
u	internal energy of unit system in the absence of motion, gravity, etc.
v	specific volume
W	net work from system
\oint	summation made around a closed cycle

GREEK LETTERS

η	thermal efficiency of heat engine
μ	Carnot's function

SUBSCRIPTS

I	irreversible process
isol.	isolated
p	constant pressure
R	reversible process

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CHAPTER IX

THE PERFECT GAS

Gases at Low Pressure and at High Temperature

At pressures that are low relative to the critical pressure, and at temperatures that are high relative to the critical temperature, the p - v - t relation for a vapor approximates the equation

$$pv = RT, \quad [18]$$

where R is a constant for any given vapor or mixture of vapors. In fact all experience with vapors indicates that this relation is a limit which the properties of a vapor approach as the pressure approaches zero or as the temperature approaches infinity. Therefore, it may often be used to represent the properties of a vapor with adequate precision.

It is shown in the following pages that the relation $pv = RT$ so restricts the specific heat at constant pressure and the specific heat at constant volume that the difference between them is constant and equal to R . It is also shown that this relation demands that lines of constant temperature should be identical with lines of constant internal energy and lines of constant enthalpy. All these conditions are approached by actual gases as they approach zero pressure.

The Universal Gas Constant

If we choose a quantity of gas or vapor which will fill volume V_0 at temperature T_0 and pressure p_0 , the volume V occupied by that same quantity of gas at any other pressure p and any other temperature T is given by the equation

$$\frac{pV}{T} = \frac{p_0V_0}{T_0},$$

provided that the pressure is very low or the temperature very high in each instance. We may also write

$$\frac{pV}{RT} = 1$$

where R denotes the quantity p_0V_0/T_0 and is the same for all gases as long as p_0 , V_0 , and T_0 are fixed.

Let us select a volume V_0 which is of such size that it will contain exactly 32 grams of oxygen at pressure p_0 and temperature T_0 . Then the amount of any gas that this volume will contain at the same pressure and temperature is called a *mole* of that gas, and its weight (under standard gravity) is called the *molecular weight* of the gas.*

Therefore, we may write

$$R = \frac{p_0 V_0}{T_0} = \frac{p_0 M v_0}{T_0} = MR, \quad [18a]$$

where M denotes the molecular weight, and R the constant for the gas of molecular weight M .

Although the quantity R is different for different gases, the quantity R is the same for all gases and is known as the *universal gas constant*. Its value as determined experimentally for the gram-molecular weight is as follows:

$$\begin{aligned} R &= 82.0618 && \text{cm}^3 \text{ atm/K g-mole} \\ &= 0.847887 && \text{kg-m/K g-mole} \\ &= 1.9857 && \text{cal/K g-mole, Btu/F lb-mole} \\ &= 1545.43 && \text{ft-lb/F lb-mole.} \end{aligned}$$

The first of these indicates that at 0 C (273.16 K) the pressure-volume product pV for one mole of a gas is given by

$$pV = 82.0618 \times 273.16 = 22,416 \text{ atm cm}^3.$$

If for any gas 1 atmosphere is a very low pressure as compared with the critical pressure, or 0 C is a very high temperature as compared with the critical temperature, then 1 gram-mole of that gas will occupy 22.416 liters at 0 C and at a pressure of 1 atmosphere. This volume is known as the *gram-molecular volume*.

The last value of the universal gas constant given above is in terms of a mixture of English and metric units. When it is divided by the molecular weight of a gas in grams per gram-mole, the value commonly tabulated, the quotient is the corresponding gas constant in English

* If the atomic weight of oxygen is made equal to one-half a molecular weight (that is, 16 grams) then the atomic weights of all other elements may be deduced from the combining weights measured in chemical reactions. It is known from experience that a mole of an element always contains a small whole number of atomic weights.

The mole proves to be a unit of significance in the interaction of different substances. For example, the same number of moles of different solutes when forming dilute solutions have in general identical effects on the vapor pressure, boiling point, and freezing point of a fixed amount of a given solution. The significance of the mole is due to the fact that a mole of a gas always contains the same number of molecules, regardless of the nature of the gas. This is a form of Avogadro's Law.

units. Thus, the gas constant for hydrogen is $1545.43/2.016$ or 766.6 ft-lb/lb F. The value of R , as determined from the universal gas constant and the molecular weight, is given with other data in Table I for a number of gases encountered in engineering.

TABLE I
DATA FOR GASES

Gas	Air	N ₂	O ₂	H ₂	CO	Hg	He	H ₂ O	Units
Mol. Wt.	28.967	28.016	32.00	2.016	28.00	200.61	4.002	18.016	lb/lb mole
R	53.35	55.16	48.3	766.6	55.18	7.70	386.2	85.8	ft-lb/lb F
c_p^*	0.240	0.248	0.217	3.445	0.249	0.025	1.25	0.47	Btu/lb F
c_v^*	0.171	0.177	0.155	2.460	0.178	0.015	0.753	0.36	Btu/lb F
k^*	1.4	1.4	1.4	1.4	1.4	1.67	1.66	1.31

* Approximate values for moderate temperatures.

Definition of a Perfect Gas — Part 1

A perfect (or ideal) gas is one having the equation of state

$$pv = RT, \quad [18]$$

where R is a constant for that gas. It was pointed out above that this equation of state is a limit which the equations of state of real gases approach as the pressure is reduced indefinitely. It fails to hold for any real gas at finite pressure. Therefore, no perfect gas actually exists, though the conclusions we draw concerning the characteristics of a perfect gas as defined above will apply with precision to real gases at low pressure or at high temperature.

To simplify further the algebra of the perfect gas it is usual to restrict its specific heats to constant values. This restriction is applied below as Part 2 of the definition. At that point the gas defined departs in characteristics from actual gases at low pressure and at high temperature, which invariably have specific heats which change with temperature. Nevertheless the change is usually gradual enough to permit the use of the equations of the perfect gas within limited ranges of temperature.

Internal Energy and Enthalpy of a Perfect Gas

The equation of state

$$pv = RT \quad [18]$$

is part of the definition of a perfect gas. Let us find some of the characteristics of a gas which conforms to it.

It has been shown previously that, for any system which in reversible processes can experience no other kind of work than that done by

pressure forces on moving boundaries, we may write for any infinitesimal change of state

$$ds = \frac{du + p dv}{T} \quad [15]$$

or

$$T ds = du + p dv.$$

Applying this to an isothermal change of state and dividing through by the increase in volume, we get

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial u}{\partial v}\right)_T + p,$$

or

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial s}{\partial v}\right)_T - p. \quad [19]$$

We may eliminate entropy from this expression in the following manner:

Consider a reversible cycle made up of two isothermals and two isometrics (constant-volume changes), and let the changes in temperature between the isothermals and in volume between the isometrics be

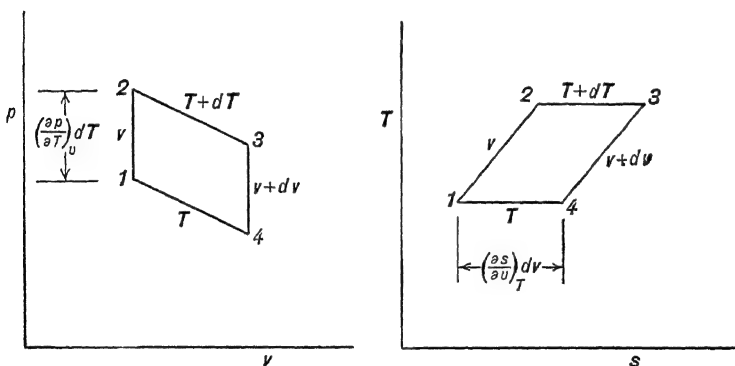


FIG. 45

infinitesimal. The net work of the cycle is the area enclosed by it on a pressure-volume diagram (Fig. 45), which, to small quantities of the second order is given by

$$\oint dW = \left(\frac{\partial p}{\partial T}\right)_v dT dv,$$

where dT denotes the change in temperature and dv the change in volume in the cycle. The net flow of heat is the area enclosed by the cycle on a temperature-entropy diagram, which is adequately stated by

$$\oint dQ = \left(\frac{\partial s}{\partial v} \right)_T dv dT.$$

In accordance with the First Law [1a], we may now write

$$\left(\frac{\partial p}{\partial T} \right)_v dT dv = \left(\frac{\partial s}{\partial v} \right)_T dv dT,$$

or simply

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v. \quad [20]$$

Substituting [20] in [19], we get

$$\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p. \quad [21]$$

Moreover, from the definition of the perfect gas [18], we get

$$\begin{aligned} \left(\frac{\partial p}{\partial T} \right)_v &= \frac{R}{v} \\ &= \frac{p}{T}, \end{aligned}$$

so that [21] becomes

$$\left(\frac{\partial u}{\partial v} \right)_T = 0. \dagger$$

Therefore, the lines of constant internal energy and the lines of constant temperature must coincide, and the internal energy must be independent of all properties except temperature: thus

$$u = f_u(T),$$

where f_u is a pure temperature function.

The definition of enthalpy is given by

$$h = u + pv,$$

which together with [18] gives

$$h = u + RT.$$

* This is one of the Maxwell relations and is proved more rigorously in Chapter XIX.

† It is easy to show that

$$\left(\frac{\partial u}{\partial p} \right)_T = -0 \cdot \frac{v^2}{RT},$$

which for finite temperature is necessarily zero only if v is finite. Therefore, as regards a real gas for which the equation of state $pv = RT$ holds only for very low pressures (very large volumes), there is no assurance that at zero pressure $(\partial u / \partial p)_T$ will vanish. Indeed, it does so only occasionally.

Since u is a function of temperature only, we may write

$$h = f_h(T),$$

where f_h is a pure temperature function. It follows that *an isothermal is a line of constant enthalpy as well as a line of constant internal energy for a perfect gas.*

Specific Heats of a Perfect Gas

The specific heats at constant pressure and at constant volume have been defined previously through the equations

$$= \left(\frac{\partial h}{\partial T} \right)_p \quad \text{and} \quad c_v = \left(\frac{\partial u}{\partial T} \right)_v$$

Since h and u are independent of pressure the partial notation may be dropped for a perfect gas. Thus,

$$c_p = \frac{dh}{dT} \quad \text{and} \quad c_v = \frac{du}{dT}. \quad [21a]$$

Referring to the definition of enthalpy, we get

$$c_p = \frac{du}{dT} + \frac{d(pv)}{dT}$$

which, with the aid of the definition of the specific heat at constant volume and the equation of state [18], may be stated in the form

$$c_p = c_v + R$$

or

$$R = c_p - c_v. \quad [22]$$

Therefore, *the difference between the specific heat at constant pressure and the specific heat at constant volume for any gas having the equation of state $pv = RT$ is equal to the gas constant R .* This statement is true for real gases at very low pressures.

If in the definitions of the specific heats given above the symbols h and u denote respectively enthalpy and internal energy per mole instead of per unit mass the specific heats are called molal specific heats. It may be readily shown that the difference between the molal specific heats, at constant pressure and at constant volume, is the same for all perfect gases and is equal to the universal gas constant.

The Ratio of the Specific Heats

A simple form of the kinetic theory of gases shows that the ratio, k , of the specific heat at constant pressure to that at constant volume is

given by the equation

$$k = \frac{c_p}{c_v} = \frac{n+2}{n},$$

where n denotes the number of degrees of freedom of the molecule.

If the molecule were merely a small rigid body the number of degrees of freedom would be the three corresponding to the directions of translation. The value of k would then be $\frac{5}{3}$ or 1.67. This value holds with good precision for monatomic gases (argon, helium, and mercury, for example) over a wide range of temperatures.

A molecule consisting of two atoms joined by some sort of bond would have two more degrees of freedom corresponding to rotation of the molecule about two axes which are perpendicular to each other and to the line joining the atoms. The corresponding value of k , $\frac{7}{5}$ or 1.4, holds with good precision over a wide range of temperatures for most diatomic gases encountered in engineering.

A molecule consisting of three or more atoms would have at least six degrees of freedom, and the value of k would therefore be $\frac{4}{3}$ or less. Thus, for the triatomic molecules H_2O and CO_2 , k is 1.31 and 1.30 respectively, whereas for ethane with eight atoms to the molecule k is 1.22.

Definition of a Perfect Gas — Part 2

It was shown above that for any gas having the equation of state [18] the internal energy is a pure temperature function. The derivative of the internal energy with respect to temperature is, therefore, a pure temperature function also. That is,

$$c_v = \psi(T),$$

where ψ is a function of temperature only.

It is customary to assume the function ψ to be a constant for a perfect gas, so that the second part of the definition of a perfect gas becomes

$$c_v = \text{constant}$$

or

$$\frac{dc_v}{dT} = 0.$$

Since the specific heat at constant pressure exceeds the specific heat at constant volume by the amount R , it follows that *for a perfect gas the specific heats at constant pressure and at constant volume are both constant for all values of any pair of independent properties.* From this and [21a]

we get for any change from state 1 to state 2

$$\left. \begin{aligned} u_2 - u_1 &= c_v(T_2 - T_1) \\ h_2 - h_1 &= c_p(T_2 - T_1) \end{aligned} \right\} \quad [22a]$$

The Reversible Adiabatic Process in a Perfect Gas

Starting once more from the familiar relation

$$T ds = du + p dv,$$

we find for the reversible adiabatic process (the isentropic process)

$$du + p dv = 0. \quad [a]$$

It was shown above that for a perfect gas

$$du = c_v dT \quad [b]$$

for any change of state. Moreover, from the equation of state [18] we get

$$dT = \frac{1}{R} (p dv + v dp). \quad [c]$$

Substitution of [b] and [c] successively into [a] gives

$$\frac{c_v}{R} (p dv + v dp) + p dv = 0.$$

Simplifying, and employing the relation

$$R = c_p - c_v,$$

we get

$$\frac{c_p}{c_v} \frac{dv}{v} + \frac{dp}{p} = 0,$$

which integrates to

$$pv^k = \text{constant}, \quad [23]$$

where

$$k = \frac{c_p}{c_v}.$$

The corresponding relations between p and T and between v and T may be found by combining [18] and [23].

In Fig. 46 the isotherm ($pv = \text{constant}$) is compared with the isentropic ($pv^k = \text{constant}$) on a p - v diagram.

The work done by a perfect gas on a piston during reversible adiabatic expansion or compression may be found as follows: For each step in the process

$$dW = p dv,$$

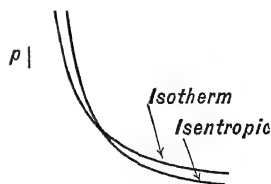


FIG. 46

or, by [a],

$$dW = -du.$$

This relation may be expressed, in view of [b] and [c], in the alternative forms

$$dW = -c_v dT$$

and

$$dW = -\frac{c_v}{R} d(pv) = \frac{-d(pv)}{k-1},$$

which integrate to

$$W = c_v(T_1 - T_2)$$

and

$$W = \frac{p_1 v_1 - p_2 v_2}{k-1}, \quad [24]$$

where subscripts 1 and 2 denote respectively the initial and final states. Since

$$p_1 v_1^k = p_2 v_2^k,$$

one v may be eliminated, the result being

$$W = \frac{p_1 v_1}{k-1} \left[1 - \left(\frac{p_2}{p_1} \right)^{(k-1)/k} \right]. \quad [25]$$

Note that each of the above expressions for W is also an expression for the integral of $p dv$.

In steady-flow problems the change in enthalpy is important. It was shown above that

$$dh = c_p dT,$$

or, by the definition of k ,

$$\begin{aligned} dh &= kc_v dT \\ &= k du. \end{aligned}$$

Following through an analysis similar to the preceding one, we get

$$h_1 - h_2 = \frac{k}{k-1} (p_1 v_1 - p_2 v_2) \quad [26]$$

or

$$h_1 - h_2 = p_1 v_1 \frac{k}{k-1} \left[1 - \left(\frac{p_2}{p_1} \right)^{(k-1)/k} \right]. \quad [27]$$

The increase in enthalpy in an isentropic process is identical with the integral of $v dp$, as is made evident by the following relations,

$$0 = T ds = du + p dv = dh - v dp;$$

therefore, the right-hand members of [26] and [27] are also expressions for the integral of $v dp$.

With the aid of [27] it is possible to compute the change in kinetic energy across a reversible adiabatic nozzle or the work done by a reversible adiabatic turbine provided that the initial state and the final pressure are known.

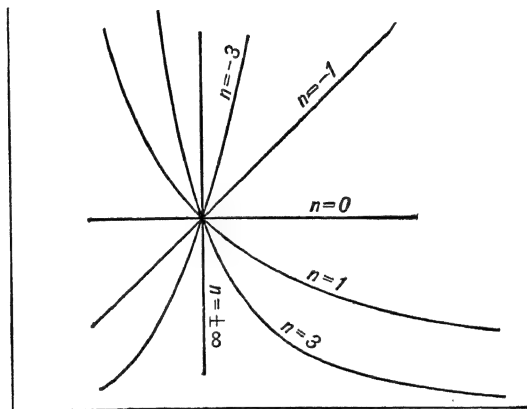


FIG. 47

The Polytropic Process in a Perfect Gas

A polytropic process is one for which the pressure-volume relation is given by

$$pv^n = \text{constant},$$

where n is a constant (Fig. 47). Either by the methods of the calculus or by comparison with [24], [25], [26], and [27] we get

$$\begin{aligned} \int_1^2 p dv &= \frac{p_1 v_1 - p_2 v_2}{n-1} \\ &= \frac{R(T_1 - T_2)}{n-1} \\ &= \left(\frac{p_1 v_1}{n-1} \right) \left[1 - \left(\frac{p_2}{p_1} \right)^{(n-1)/n} \right], \end{aligned} \quad [28]$$

and

$$\begin{aligned} \int_1^2 v dp &= \frac{n(p_2 v_2 - p_1 v_1)}{n-1} \\ &= \frac{nR(T_2 - T_1)}{n-1} \\ &= -p_1 v_1 \frac{n}{n-1} \left[1 - \left(\frac{p_2}{p_1} \right)^{(n-1)/n} \right] \end{aligned} \quad [29]$$

The first of these is the work done by the system in a reversible polytropic process, but it is not in general equal to the decrease in internal energy. The second is the increase in kinetic energy across a reversible nozzle or the work delivered by a reversible turbine in steady flow, but it is not in general equal to the increase in enthalpy.

A convenient expression for the transfer of heat in a reversible polytropic process may be derived as follows:

$$Q = u_2 - u_1 + \int_1^2 p \, dv,$$

which, by [28] and the expression for c_v , becomes

$$Q = \left(\frac{R}{n-1} - c_v \right) (T_1 - T_2)$$

or

$$Q = \frac{c_p - nc_v}{n-1} (T_1 - T_2).$$

Expressions for Q in terms of the pressure-volume product or of the initial pressure and temperature and the pressure ratio may be derived from this last equation.

Entropy of a Perfect Gas

Changes in the entropy of a perfect gas may be found through the relation

$$ds = \frac{du}{T} + \frac{p \, dv}{T},$$

which is readily transformed for the present case into the following forms:

$$\begin{aligned} ds &= c_v \frac{dT}{T} + R \frac{dv}{v} \\ &= c_v \frac{d(pv)}{pv} + R \frac{dv}{v} \\ &= c_p \frac{dv}{v} + c_v \frac{dp}{p} \\ &= c_p \frac{dT}{T} - R \frac{dp}{p}. \end{aligned}$$

The corresponding integral relations are

$$\begin{aligned}
 s_2 - s_1 &= c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \\
 &= c_v \ln \frac{p_2 v_2}{p_1 v_1} + R \ln \frac{v_2}{v_1} \\
 &= c_p \ln \frac{v_2}{v_1} + c_v \ln \frac{p_2}{p_1} \\
 &= c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1}.
 \end{aligned} \tag{31}$$

If we choose to make the entropy zero at some reference state 0, then the entropy s at any other state is given, for example, by

$$s = c_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0},$$

where p and T are the pressure and temperature of the state in question, and p_0 and T_0 are the corresponding quantities for the reference state 0. An equivalent expression is

$$s = c_p \ln T - R \ln p + s', \tag{32}$$

where s' is a constant.

The increase of entropy during a polytropic process is readily shown to be given by

$$s_2 - s_1 = \frac{c_p - n c_v}{n - 1} \ln \frac{T_1}{T_2}.$$

PROBLEMS

1. Determine the gas constant in ft-lb/lb F abs for acetylene gas, C_2H_2 .

2. Find the number of pounds of N_2 , O_2 , H_2 , CO , Hg , He , and H_2O that would be held by a container of 10 cu ft volume at a temperature of 300 F and at a pressure of 1 atmosphere (assuming that each of these gases is a perfect gas). Find the corresponding number of moles of each.

Compare the number of pounds of H_2O found in this calculation with the number that would be found using values from the *Steam Tables*.

3. (a) Find the work done by 1 lb of hydrogen on a piston when the hydrogen expands isothermally at 1000 F abs from 100 lb/sq in. abs to 10 lb/sq in. abs.

(b) Find the work done by a volume of hydrogen which is initially the same as in (a), when it expands isothermally at 500 F abs through the same range of pressure. Compare the work done per pound of hydrogen in the two cases.

(c) Find the heat transferred in (a) and (b).

4. A constant-volume container holds 32 lb of oxygen and 12 lb of solid carbon. It is surrounded by a liquid bath which is maintained at a constant temperature of 200 F. The carbon is ignited and burns completely.

Find the final pressure of the gas in the container if the initial pressure is 1 standard atmosphere. Assume that the initial volume of the solid carbon is negligible and that in the final state the gas is in temperature equilibrium with the liquid bath.

5. If, instead of oxygen and carbon, a container similar to that of problem 4 had held 32 lb of oxygen and 4.03 lb of hydrogen, what would be the final pressure after complete combustion? (Assume the same temperature and initial pressure as given above.)

6. Measurements on a certain perfect gas at 600 F abs show that the specific heat at constant pressure is 0.327 and that at constant volume 0.256 Btu/lb F. It is also found that at 38.32 lb/sq in. abs the specific volume of the gas increases by 0.01 ft³/lb for each degree F increase in temperature.

From these data, compute the number of foot-pounds in 1 Btu.

7. Find the work done by, the heat received by, the increases in internal energy, enthalpy, and entropy of a closed system consisting of 1 lb of air which is initially at 20 lb/sq in. abs and 600 F abs as its volume doubles in the following processes:

- (a) Reversible constant pressure.
- (b) Reversible constant temperature.
- (c) Reversible constant internal energy.
- (d) Reversible constant enthalpy.
- (e) Reversible constant entropy.
- (f) Adiabatic expansion into an exhausted chamber.
- (g) Reversible $pv^2 = \text{constant}$.
- (h) Reversible $p/v = \text{constant}$.

8. An unknown mixture of diatomic gases ($k = 1.4$) initially occupies a volume of 100 cu ft at 10 lb/sq in. abs and 100 F. If in a reversible process the temperature is increased to 200 F while the pressure remains constant, find the work done and the heat received by the gas and the increases in its volume, internal energy, enthalpy, and entropy.

9. What is the possible range of values of n for adiabatic and polytropic expansion of a perfect gas provided that no work is supplied from the surroundings?

10. Derive by the methods of the calculus expressions for $\int p dv$ and $\int v dp$ between a state corresponding to p_1, v_1 and a state corresponding to p, v for a path for which $pv^n = \text{constant}$.

11. Compute the change in internal energy, enthalpy, and entropy for a mass of a monatomic gas ($k = \frac{5}{3}$) when it changes in pressure from 5 to 10 lb/sq in. abs and in temperature from 1000 to 800 F abs. The original volume of the gas is 1 cu ft.

12. Air is compressed reversibly in the cylinder of a compressor according to the relation

$$pv^{1.3} = \text{constant}.$$

Find the net heat transfer to each pound of air (to is +, from is -) if:

- (a) The temperature of the air increases by 100 F.
- (b) The initial pressure is 10 lb/sq in. abs, the initial temperature 500 F abs, and the final pressure 20 lb/sq in. abs.

13. Find expressions for the entropy of a perfect gas similar to

$$s = c_p \ln T - R \ln p + s'$$

in terms of p and v , T and v , and pv and p .

14. Sketch a T - s diagram for a perfect gas showing lines of constant p , v , u , and h .
Is a constant- p line convex up or down? Why?
Is a constant- v line convex up or down? Why?

Show that $s_2 - s_1 = \frac{c_p - nc_v}{n-1} \ln \frac{T_1}{T_2}$ for a polytropic process.

15. A mass of air which occupies 1 cu ft under a pressure of 100 lb/sq in. abs is expanded at constant pressure until its volume is 3 cu ft. Next it undergoes a polytropic expansion until its pressure is 15 lb/sq in. abs and its volume is 6 cu ft. It is restored to its initial state by means of an isothermal compression and an adiabatic compression. All these processes are executed reversibly.

- Determine the heat received from the source and the heat rejected to the sink if only one source and one sink are available. Find the efficiency of the cycle.
- Assume the initial temperature to be 500 F abs and solve the problem using relationships involving specific heats.
- Can we assume any values of the initial temperature or of the mass of air and get the same results?
- How would the results differ, if at all, if the gas were nitrogen instead of air?

16. A horizontal insulated cylinder contains a frictionless non-conducting piston. The area of the piston is 1 sq ft. On each side of the piston is 1 cu ft of air at 20 lb/sq in. abs and 40 F. Heat is slowly supplied to the air on the left side until the piston has compressed the air on the right side to 100 lb/sq in. abs.

- How much work is done by the air on the right side?
- How much heat is added to the air on the left side?
- Can we treat the expansion of the air on the left side as a polytropic expansion and obtain the correct results?
- What is the p - v relation for the air on the left side? Find the work done by that air with the aid of this relation.

17. A semi-perfect gas is one that satisfies part 1 of the definition of a perfect gas but not part 2. For one such gas we have the relation

$$c_p = 9.47 - \frac{3.47 \times 10^3}{T} + \frac{1.16 \times 10^6}{T^2} \quad \text{Btu/F mol.}$$

The molecular weight of the gas is 28.

- How much heat is required to raise the temperature of 1 lb of the gas from 500 to 5000 F abs reversibly if the pressure is constant? if the volume is constant?
- What is the average value of k in this range?

18. A steady stream of air enters a compressor at low velocity at a pressure of 15 lb/sq in. abs and at a temperature of 70 F, and leaves at low velocity at a pressure of 150 lb/sq in. abs and a temperature of 600 F. If no net heat transfer occurs to or from the air as it passes through the compressor, what is the magnitude of the work done on each pound of air by the compressor?

19. A steady stream of air enters a reversible adiabatic compressor at low velocity at a pressure of 15 lb/sq in. abs and at a temperature of 70 F, and leaves at low velocity at a pressure of 150 lb/sq in. abs. Find the amount of work done on each pound of air by the compressor and the temperature of the air leaving the compressor.

20. Starting from the steady-flow energy equation show that the velocity, V , of a perfect gas leaving a frictionless adiabatic nozzle is given by the expression

$$V = \sqrt{2g p_1 v_1 \frac{k}{k-1} \left[1 - \left(\frac{p}{p_1} \right)^{(k-1)/k} \right]},$$

where subscript 1 refers to the state at the cross section corresponding to zero velocity and p denotes the pressure at the exit section of the nozzle.

21. Find an expression for the flow of a perfect gas through unit cross-sectional area of a frictionless adiabatic nozzle in terms of the pressure at the section in question and the temperature and pressure at the section where the velocity is zero.

22. Find for a perfect gas an expression for the ratio of the pressure at the throat (cross section of minimum area) of a frictionless adiabatic nozzle to the pressure at the section where the velocity is zero. Tabulate values of this pressure ratio for values of k between 1.2 and 1.7.

23. A perfect gas flows *adiabatically* through a long pipe of *constant cross-sectional area*. At one cross section the properties and the velocity are known and may be denoted by symbols with subscript 0 — p_0, T_0, \dots, V_0 . Downstream from this section the pressures are lower and upstream they are higher than p_0 by virtue of frictional resistance to the flow of the gas.

(a) Find a relationship between the enthalpy, h , and the specific volume, v , at any cross section of the pipe in terms of properties and velocity at section 0.

(b) Find a similar relation between pressure, p , and specific volume, v .

(c) Find a similar relation between enthalpy, h , and entropy, s .

Assume the gas to be air, the pressure p_0 10 lb/sq in. abs, the temperature T_0 1000 F abs, and the velocity V_0 1000 ft/sec. Plot the path of states from zero pressure to the highest possible pressure on h - v , p - v , h - s , and T - s diagrams.

SYMBOLS

c_p	specific heat at constant pressure
c_v	specific heat at constant volume
f_u, f_h	pure temperature functions
h	enthalpy per unit mass
M	molecular weight
n	number of degrees of freedom
p	pressure
Q	heat to system
R	gas constant
R	universal gas constant
s	entropy per unit mass

T	temperature, absolute
u	internal energy of a unit system in the absence of motion, gravity, etc.
v	specific volume
V	volume
W	work from system

GREEK LETTER

ψ	function of temperature
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SUBSCRIPT

v	constant volume
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CHAPTER X

THE RECIPROCATING STEAM ENGINE

The devices that are commonly called steam engines, namely, the reciprocating engine and the turbine, are not, in the thermodynamic sense, heat engines, but parts of heat engines. A heat engine was defined on page 58 as a continuously operating system across whose boundaries flow only heat and work. A reciprocating engine or a turbine, on the other hand, has a flow of steam across its boundaries. It should be noted also that a flow of heat is not essential to the operation of a reciprocating engine or a turbine — in fact, the idealized engine or turbine is an adiabatic device.

A brief description of a heat engine of which a turbine forms a part was given on page 62 and in Fig. 30. Let us follow the course of a unit mass of water as it passes around the circuit. The fluid is in the liquid phase at 1, which is the entrance to the boiler, at a pressure slightly above that at 2, which is the exit from the superheater. Through the turbine a large fall in pressure and temperature occurs to the state at 3. Between the exit from the turbine, 3, and the condensate line, 4, the cool steam is condensed to cool liquid at only slightly lower pressure. The liquid is then raised in pressure with only slight change in temperature by the pump which restores the initial state 1.

The changes in pressure that occur in the boiler and superheater and in the condenser are not essential to the operation of the heat engine and are in fact undesirable. Therefore, in the idealized cycle we may assume them to vanish. Similarly, all friction and transfer of heat in the turbine and the pump may be assumed to vanish so that the change of state of a given mass of fluid as it passes through these devices is reversible and adiabatic. Thus, the idealized cycle consists of two constant-pressure processes and two isentropic processes. It is called the *Rankine cycle*. In Fig. 48 it is shown by solid lines on the pressure-volume plane and on the temperature-entropy plane. In the latter the area under curve 1-2 is the heat added in the boiler and superheater to unit mass of fluid, and the area under curve 3-4 is the heat rejected to the condenser by unit mass of fluid, in accordance with the definition of entropy. In both diagrams the enclosed area 1-2-3-4-1 is the net work

$(W_e - W_p)$ delivered by each unit mass of fluid passing through the cycle.

The dash lines in the diagrams show an actual cycle having the same states at turbine inlet and at pump inlet as in the idealized cycle. In place of the isopiestic of the idealized cycle we have lines of falling pressure, and in place of the isentropics, lines of increasing entropy.

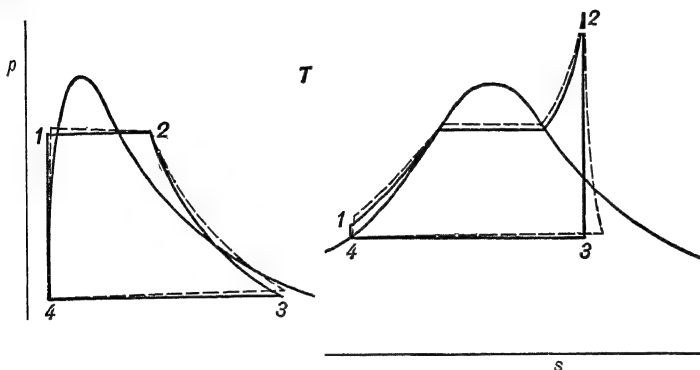


FIG. 48

The Reciprocating Engine

The reciprocating engine, like the turbine of Fig. 30, is a device which delivers work when provided with a supply of fluid at high pressure and a region of low pressure into which the fluid may be exhausted. It normally comprises, as in Fig. 49, a cylinder c , closed by a piston p , which is connected by means of a piston rod r and connecting rod k to a

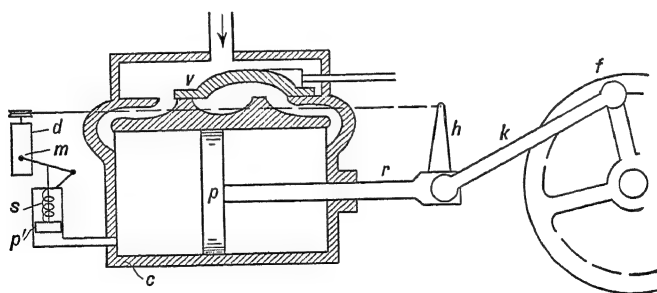


FIG. 49. Reciprocating Engine

flywheel f , and a valve mechanism v for admitting and discharging fluid at appropriate times in the course of its cycle of operations.

For thermodynamic analysis of the processes executed by the working fluid two kinds of measurements are employed: first, a measurement of the rate of flow of fluid to or from the engine; second, a record of the

relationship between pressure of the working fluid and position of the piston. This record is known as an *indicator diagram* and is obtained from a device called an *indicator*. The two coordinates of an indicator diagram are pressure and position of the piston. The pencil *m*, Fig. 49, which draws the diagram on a card, is caused to move vertically a distance proportional to the pressure on the cylinder wall by means of a small piston *p'*, which is exposed to the pressure within its own cylinder and whose motion is resisted by a calibrated spring *s*. The card is mounted on a drum *d*, which is caused to rotate (by means of a cord and a reduction gearing which connects with the crosshead *h*), so that its angular displacement is proportional to the motion of the piston.

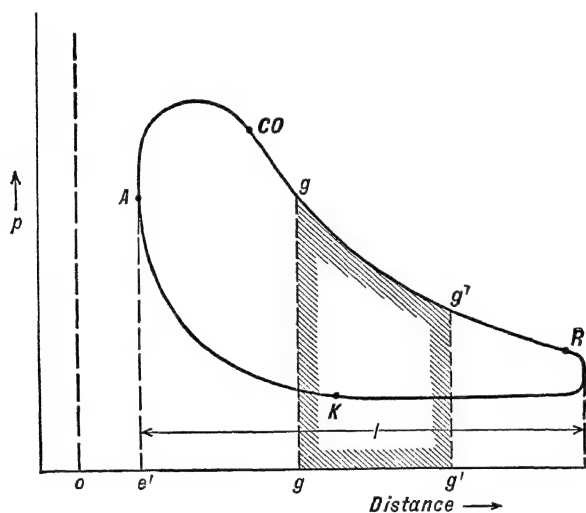


FIG. 50. Indicator Diagram

A typical diagram is shown in Fig. 50. The positions of the piston corresponding to the ends of the card, e' and e'' , are known as the *dead-center* positions. It is easily seen that the volume swept through by the face of the piston between dead center, e' , and any position, g , is proportional to the distance, $e'g$. The volume of fluid confined within the engine between valve and piston is the volume measured by $e'g$, where g denotes the position of the piston, plus the volume so confined when the piston is at dead center e' . The volume confined when the piston is at e' is called the *clearance volume* and comprises the portion of the cylinder volume not swept through by the piston in its stroke and the volume of ports or passages between valve and cylinder. To the scale to which the abscissa of the diagram indicates displaced volume

we may lay off the clearance volume, oe' , to the left of e' . Then to the same scale the distance og measures the volume of fluid confined between valve and piston. If the mass of fluid that is confined is known, then it is possible by means of the distance og and the scale factor to determine the specific volume of the fluid.

The work done by the fluid on the piston as it moves from g to g' is represented by the area under the curve joining the corresponding points on the indicator diagram. Moreover, the area enclosed by the diagram represents the net work delivered to the piston in the course of one cycle of operations.

Four *events* are commonly marked on an indicator card: admission, A , at the point where the inlet valve opens; cutoff, CO , at the point where the inlet valve closes; release, R , where the exhaust valve opens; and compression, K , where the exhaust valve closes. Barring leakage past valves and piston, the mass of fluid confined between cutoff and release is constant, and the same is true between compression and admission. The quantity of steam confined within the engine between compression and admission is known as the *cushion steam*. The quantity of steam that enters the cylinder between admission and cutoff (and that leaves between release and compression for steady conditions) is called the *flow steam*. The quantity of steam confined within the engine between cutoff and release is the sum of the cushion steam and the flow steam.

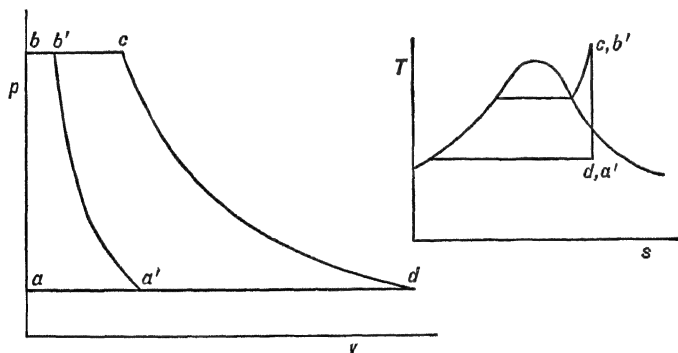


FIG. 51. Diagrams for the Reversible Adiabatic Engine

Indicator Diagram of a Reversible Adiabatic Engine

A reciprocating engine in which all processes are reversible must be free from any fall in pressure across the valves during admission and during exhaust, and it must be free from transfer of heat to and from the fluid. The indicator diagram for such an engine without clearance is shown by the line $abcda$ in Fig. 51. The pressure along bc is the pressure

in the supply main, and that along ad is the pressure in the exhaust chamber. The expansion line cd follows the pressure-volume relation of an isentropic expansion.

The indicator diagram for a reversible adiabatic engine with clearance is given by $a'b'cda'$. The process represented by $a'b'$ is isentropic and follows, in fact, the same series of states, but in inverse order, as process cd ; that is, process $a'b'$ is precisely the reverse of process cd , except that a smaller amount of fluid is involved.

Effects of Irreversibility

In an actual engine some pressure drop must occur between the supply main and the cylinder and between the cylinder and the exhaust chamber, so that the indicator diagram of the actual engine (the dash line of Fig. 52) is of lesser height than that of the reversible engine.

In the actual engine the exhaust valve is opened while the fluid is at a pressure (corresponding to R) which is distinctly higher than the pressure in the exhaust chamber. The engine is then said to have *incomplete expansion*. Friction between piston and cylinder and between moving parts and bearing surfaces will absorb some work for

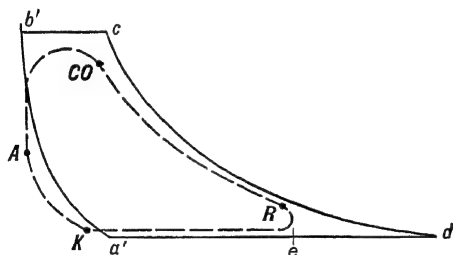


FIG. 52

each increment of the piston stroke; and, if the net work done by the fluid on the piston over that increment is less than the work absorbed, it is better to eliminate that part of the stroke. Thus, the stroke usually ends at some point e which is short of the point of complete expansion d .

Similar considerations dictate *incomplete compression* to a pressure (corresponding to A) which is distinctly less than the pressure in the supply chamber (corresponding to $b'c$). The course of the expansion line $CO-R$ departs from the isentropic principally because of heat transfer between the fluid and the cylinder walls. Engine cylinders are adequately insulated, as a rule, from their environment, so that no significant amount of heat leaves the engine. But transfer of heat may occur from steam to walls in the high-pressure parts of the operation when the steam is hot, and from walls to steam in the low-pressure parts when the steam is cold. This exchange of heat is an irreversible process which will be analyzed in detail later.

Steady-Flow Analysis

Because the reciprocating engine passes through a cycle of operations it can be studied through the energy equation of steady flow. For steady conditions at the inlet and outlet there must be enough volume of fluid between the engine and the points of measurement to absorb fluctuations that are caused by the intermittent nature of the operations of the engine.

Consider a reciprocating engine having receivers in the inlet and discharge lines (Fig. 53) that are large enough to insure steady conditions at a section 1 preceding the inlet receiver and at a section 2 following the discharge receiver. For steady flow into and out of this apparatus we may write [6] in the form

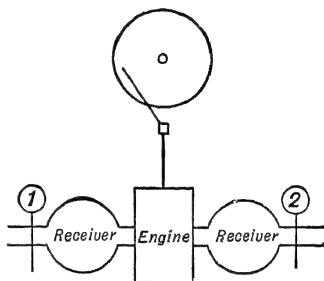


FIG. 53

$$h_1 + \frac{V_1^2}{2g} = h_2 + \frac{V_2^2}{2g} + W_x - Q, \quad [33]$$

where h denotes the enthalpy per unit mass of fluid, V the mean velocity, W_x the work delivered by the engine per unit mass of fluid entering at 1, and Q the heat entering the fluid from outside per unit mass of fluid entering at 1. In general, $V^2/2g$ is small at 1 and 2; moreover, Q is seldom of significant magnitude. Therefore, [33] becomes

$$h_1 = h_2 + W_x. \quad [34]$$

If two of the three quantities h_1 , h_2 , and W_x are known the third follows from [34]. If the steam at 1 is superheated, measurements

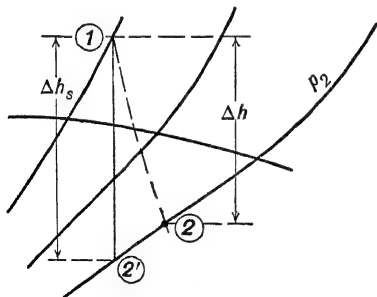


FIG. 54

of pressure and temperature will suffice to determine h_1 . Commonly, a two-phase mixture of liquid and vapor is found at 2 so that the value of h_2 does not follow from measurements of pressure and temperature only. But it may be determined from either of these measurements if the change of state from 1 to 2 is reversible (as well as adiabatic). For then the entropy of state 2 is identical with the known entropy of

state 1, and the combination of entropy and pressure or of entropy and temperature identifies state 2. Thus, on the enthalpy-entropy dia-

gram of Fig. 54, Δh_s denotes the work delivered by each pound of steam to the piston of a reversible adiabatic engine, which receives steam at state 1 and exhausts it at pressure p_2 . The state, 2', in Fig. 54 is the condition of steam leaving the reversible engine.

The state of the steam leaving an actual engine, 2, will be different from the state of the steam leaving a reversible engine, 2'. By the principle of the increase of entropy, the entropy of state 2 must be greater than that of state 1, so that the work per pound of steam, which by [34] is the Δh of Fig. 54, is less than the work per pound of steam of the reversible engine.*

Efficiency of an Engine

The *efficiency* of an engine of either the reciprocating type or the turbine type is defined by the equation

$$\eta = \frac{W_x}{W_r}, \quad [35]$$

where η denotes the efficiency, W_x the work delivered per pound of steam flowing to the engine, and W_r the work delivered by a reversible adiabatic engine working between the same inlet state and the same final pressure (but not the same final state) as the actual engine. For an adiabatic engine with negligible velocities in the supply and discharge mains [35] becomes

$$\eta = \frac{\Delta h}{\Delta h_s}.$$

It should be noted that the efficiency of a reciprocating engine or turbine is different from the efficiency of a heat engine, which is the ratio of work delivered to heat received. Neither the reciprocating engine nor the turbine depends for its operation on a transfer of heat — otherwise the discussion above would not be limited to adiabatic engines. For this reason, the efficiency of a heat engine and the efficiency of a reciprocating engine need never be confused, because the definition of the former cannot be applied either to a reciprocating engine or to a turbine. Furthermore, the efficiency of a heat engine is usually of a smaller magnitude than the efficiency of a reciprocating engine — the former being commonly less than 50 per cent and the latter commonly greater.

* This is evident from Fig. 54 in which the lines of constant pressure have positive slope. An expression for the slope is found as follows:

$$ds = \frac{du + p dv}{T} = \frac{dh - v dp}{T},$$

so that $(\partial s / \partial h)_p = 1/T$, which is always positive.

Cylinder Condensation

When steam passes through the ports of a reciprocating engine on its way to the cylinder, it flows by walls which have been cooled but a moment before by steam passing to the exhaust port. The conditions being favorable, a large transfer of heat occurs from steam to walls. The steam is thereby cooled and sometimes a large portion of it is condensed, while the walls are heated. The consequences of this transfer of heat are therefore said to be the results of cylinder condensation.

When, with the exhaust stroke, cold steam flows past these walls once more, the steam is heated and the walls are cooled. Barring transfer of heat to the atmosphere, the net flow of heat through a cycle of operations is zero, and all conclusions that apply to a finite adiabatic process will apply to the process experienced by the steam while passing through the engine.

The transfer of heat from the steam in its hot state to the wall and from the wall to the steam in its cold state is inherently irreversible. Therefore, in accordance with Corollary 6 of the Second Law, the entropy of the steam is greater when it leaves the engine than when it enters. It follows that the enthalpy of the steam leaving the engine is greater than it would have been had the process been reversible, and the work delivered by the engine is less by the amount that the enthalpy is greater. This loss of work is readily accounted for by a reduction in pressure and volume after admission and an increase in these quantities after release. The dash and solid lines of the indicator diagram of Fig. 55 indicate respectively operation with and without transfer of heat. The effects are important enough to justify a further analysis which is named after Hirn who presented it in 1876.

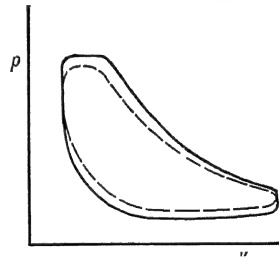


FIG. 55

Hirn's Analysis

The state of the steam in the cylinder at any instant may be determined from the coordinates of the corresponding point on the indicator diagram if the mass of the steam in the cylinder is known. For, the ratio of volume (the abscissa) to mass is the specific volume, which with the pressure (the ordinate) determines the state.

It is not easy to measure the mass of the "cushion steam" that occupies the cylinder between compression K and admission A , but an approximation which is generally satisfactory can be obtained by assuming a saturated vapor state at K . The mass of steam in the

cylinder at any point between cutoff, CO , and release, R , is then the sum of the cushion steam and the flow steam per stroke, the latter being found by measuring the mass of condensate leaving the condenser in the time required for one stroke. (It is assumed, of course, that leakage past the piston is negligible.)

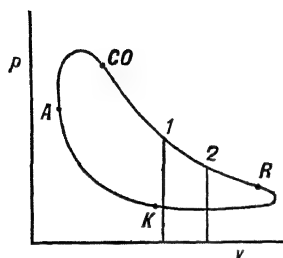


FIG. 56

With this value of the mass it is possible to find the state of the steam corresponding to any position of the piston between CO and R . All properties for such a state may be found from the *Steam Tables*.

For the change in state between two positions of the piston such as 1 and 2, Fig. 56, we may write [2a] in the form

$$Q = m(u_2 - u_1) + W,$$

where m denotes the mass of steam in the cylinder. The work, W , is found readily from the area under the curve 1-2 on the indicator diagram. The heat, Q , is the transfer from walls to steam and will be negative at the CO end of the curve. A similar analysis may be made of transfer of heat for the operation between K and A .

Between A and CO the mass within the cylinder is not constant. We may, however, describe a closed system comprising all the fluid confined between valve and piston at CO . In state A corresponding to admission the system is divided into two parts, each of which may be assumed uniform in state: the part consisting of the cushion steam w_c which is confined between valve and piston (Fig. 57), and the part consisting of the flow steam w_f which is in the steam main at state m . For the change from A to CO we may write [2a] in the form

$$Q = (w_c + w_f)u_{CO} - (w_c u_A + w_f u_m) + W.$$

The work W includes the positive work done by the system on the piston and the negative work done on the fluid in the steam main. To make this latter work more evident we may imagine the fluid following mass w_f to be replaced by a piston (P' , Fig. 57). In order to maintain steam-main pressure it is necessary to apply a force to P' equal to the product of its area and the steam-main pressure p_m . Now as the steam flows into the cylinder the work done on the system is given by $w_f p_m v_m$. If we let ${}_A W_{CO}$ denote work done on the piston of the

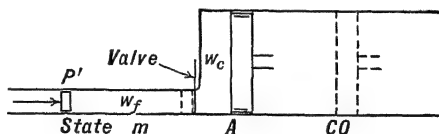


FIG. 57

engine between admission and cutoff, the last equation becomes

$$Q = (w_c + w_f)u_{CO} - (w_c u_A + w_f u_m) - w_f p_m v_m + {}_A W_{CO}, \quad [36]$$

or

$$Q = (w_c + w_f)u_{CO} - (w_c u_A + w_f h_m) + {}_A W_{CO}. \quad [37]$$

Similarly, it may be shown that the heat transferred to the steam between release and compression is given by

$$Q = w_c u_K + w_f h_0 - (w_c + w_f)u_R + {}_R W_K, \quad [38]$$

where h_0 denotes the enthalpy per unit mass in the exhaust main and ${}_R W_K$ the work done by the steam on the piston of the engine between release and compression.

The analyses of these last two cases can be stated briefly if the equation for an open system [5] is first simplified by omitting the terms representing kinetic energy and height. Thus

$$\delta Q = E'' - E' - h\delta m + \delta W_x, \quad [39]$$

where δQ denotes the heat transferred to the open system while mass δm enters, δW_x the corresponding work done on the piston of the engine, and E' and E'' respectively the internal energies of the masses initially and finally within the cylinder. It is easy to see that [39] becomes [37] and [38] for the two processes analyzed above.

The summation of the quantities of heat corresponding to the four processes joining the four events should vanish, within the limits of error of the method, for all engines of ordinary size. For very small engines the summation should be negative and equal to the heat loss from the engine to the atmosphere per cycle of operations.

Methods of Reducing Cylinder Condensation

The losses caused by transfer of heat or cylinder condensation in the ordinary reciprocating steam engine are large enough in many instances to justify the following modifications of the usual procedure and design:

Superheating. The higher the temperature of the steam entering the cylinder, the less will be the moisture present during the exhaust stroke. The resistance to transfer of heat at this end of the cycle of operations is therefore much greater and the fall in the temperature of the walls much less. The incoming steam, being exposed to hotter walls, gives up less heat to them.

Corliss Valves. Steam entering and leaving the cylinder moves at high velocity past port walls, and it is to these walls, therefore, that much of the heat transfers. The simple slide-valve mechanism in

which all action of the valve is concentrated on one side of the cylinder involves long ports with large surfaces which facilitate transfer of heat. Separate exhaust valves and inlet valves have been devised, of which the Corliss valves are examples, which can be placed close against the end of the cylinder so as to reduce the area of port walls to a minimum.

Compounding. If the expansion is subdivided into two parts (Fig. 58) which the steam executes successively in separate cylinders (a high-pressure cylinder and a low-pressure cylinder), the change in tem-

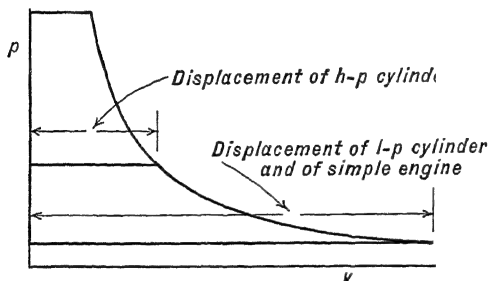


FIG. 58

perature experienced by the steam in one cylinder may be cut in half. The differences in temperature between steam and walls are in turn cut in half. On the other hand, the wall surface to which the steam is exposed is not doubled, since the low-pressure cylinder is of the same dimensions as the simple engine (Fig. 58) whereas the high-pressure cylinder is much smaller. Therefore the transfer of heat between steam and walls is reduced.

This modification of the engine is called compounding. It has been extended to as many as five expansions in series, though more than three is uncommon.

Uniflow. The uniflow engine reduces cylinder condensation by eliminating the usual reversal in the direction of the flow of steam between admission and exhaust. Incoming steam passes over the end of the cylinder (Fig. 59) and enters through an admission valve. When the face of the piston has moved almost to the middle of the cylinder it uncovers exhaust ports through which the steam leaves the cylinder. The piston is long enough to close the exhaust ports over most of its stroke.

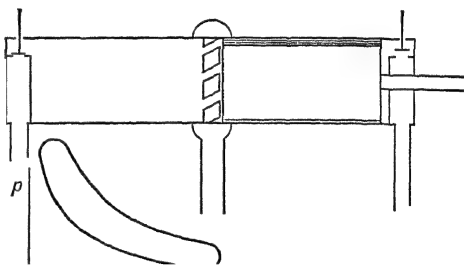


FIG. 59. The Uniflow Engine

By virtue of the uniflow design hot steam never comes in contact with the middle parts of the cylinder and cold steam never flows past the hot ends of the cylinder. Even for large ranges of temperature the transfer of heat to and from the walls is small.

PROBLEMS

In the following problems the events (CO , R , K , and A) are expressed in terms of percentage of the stroke which separates the piston from its extreme position (dead-center position) at the compression end. Thus, if CO were 20 per cent and K were also 20 per cent, these two events would occur with the piston in the same position, though for the first it would be moving outward and for the second it would be moving inward. Note that the volume confined by the piston at either of these events would be the sum of the clearance volume and 20 per cent of the piston displacement.

The clearance is often expressed as a percentage of the piston displacement.

A double-acting engine is one in which steam is admitted alternately to the two sides of the piston. Other things being the same, a double-acting engine produces approximately twice as much work as a single-acting engine.

1. Find the quality of steam at cutoff in a cylinder in which the piston displacement is 0.1278 cu ft, clearance 10 per cent, cutoff 25 per cent, steam pressure at cutoff 115 lb/sq in. abs, and weight of steam in cylinder at cutoff 0.012 lb.

2. Find the weight of cushion steam in a 6-in.-diameter, 8-in.-stroke engine in which clearance is 15 per cent, and compression begins at 20 per cent. The back pressure (exhaust-chamber pressure) is 14.7 lb/sq in. abs. Assume, as usual, dry saturated steam at the beginning of compression.

Find also the pressure and quality or superheat at the end of the compression, assuming reversible adiabatic compression.

3. Suppose that the compression in the previous problem is not adiabatic, but such as to produce a final pressure of 35 lb/sq in. abs. Find the quality or superheat of the cushion steam at the end of compression.

4. An 8-in.-diameter, 10-in.-stroke, double-acting engine running 300 rpm, with cutoff at 15 per cent and at 120 lb/sq in. abs, requires 35 lb of steam per ihp-hr. Compression starts at 40 per cent and at 5 lb/sq in. abs. Clearance is 10 per cent. The indicated power is 30 hp.

(a) Find weight of cushion steam and of flow steam per stroke.

(b) Find quality at cutoff.

(c) Assuming release to occur at 90 per cent and at 30 lb/sq in. abs, find quality at release.

5. An engine is supplied with dry saturated steam at 150 lb/sq in. abs and exhausts to a surface condenser at 5 lb/sq in. abs.

When running without a steam jacket, the engine requires 20 lb of steam per ihp-hr.

When running with a jacket, it requires 18 lb per ihp-hr for the cylinder, and 2 lb per ihp-hr for the jacket.

Assuming jacket pressure as 150 lb/sq in. abs and no loss of heat from piping, find:

(a) Heat added in the boiler in Btu per ihp-hr for each case.

(b) Efficiency of the complete heat engine in each case.

(c) Per cent saving due to jacket.

6. (a) Find the indicated work per pound of steam for a reversible adiabatic engine which receives steam at 100 lb/sq in. abs and 400 F and rejects it to a condenser at 5 lb/sq in. abs.

(b) Find the indicated work if the steam were throttled to 75 lb/sq in. abs before being introduced into the engine.

(c) Sketch indicator cards for (a) and (b).

7. Show by reduction-to-absurdity methods that the work per pound of steam in a reversible adiabatic reciprocating engine is greater than that of an actual adiabatic engine which receives steam in the same state and rejects it at the same pressure.

8. *Engine:*

Double-acting, 200 rpm, 8-in.-diameter, 10-in.-stroke (p.d. = 0.291 cu ft).

Supply steam: 125 lb/sq in. abs, dry saturated.

Condenser: 14.7 lb/sq in. abs. Cooling water, 30 lb/lb steam; inlet temperature: 65.00 F; outlet temperature: 95.97 F; steam flow: 0.02293 lb/stroke; condensate temperature: 200 F.

Events:

Cutoff	(CO) = 20 per cent, 110 lb/sq in. abs.
Release	(R) = 95 " " 32 " " " "
Compression	(K) = 30 " " 20 " " " "
Admission	(A) = 0 " " 80 " " " "

Clearance = 10 per cent.

Assume as usual dry saturated steam at K .

Work (positive when done by the steam):

A to CO	1.239 Btu/stroke
CO to R	2.222 " "
R to K	-0.711 " "
K to A	-0.597 " "

Net work 2.153

(a) What is the weight of cushion steam?

(b) What is the quality at cutoff?

How much heat is transferred, and in which direction, between:

(c) Admission and cutoff?

(d) Cutoff and release?

(e) Release and compression?

(f) Compression and admission?

(g) What is the net heat transfer from the cylinder to the surroundings?

(h) What is the efficiency of the engine?

(i) Is the work per pound of flow steam equal to the change in enthalpy between the steam main and the condenser inlet?

9. The *mean effective pressure* (mep) on a piston is that pressure which when multiplied by the area of the piston and the stroke gives the net work done on the piston in one cycle of events. Find the mep corresponding to the data of problem 8.

10. A *conventional indicator card* (Fig. 60) consists of a line of constant pressure corresponding to the pressure in the steam main and extending between zero volume and the volume at cutoff, a line for which pV is constant extending from the volume at cutoff to the volume confined by the piston at the end of its travel, a line of constant volume at this latter volume extending downward to the condenser pressure, and a line of constant pressure extending to zero volume. Find an expression for the mep of the conventional indicator card in terms of the steam-main pressure, p_m , the condenser pressure, p_c , and the ratio of the maximum volume to the volume at cutoff (the expansion ratio), R .

11. The diagram factor is the ratio of the mep of an actual indicator card to that of the corresponding conventional indicator card. Tables of values of diagram factors that correspond to the performance of engines of different types under various conditions may be found in engineers' handbooks. An example of the application of the diagram factor is given in the following problem:

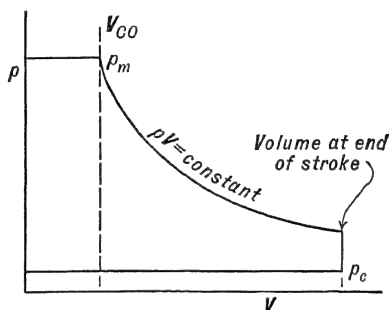


FIG. 60. Conventional Indicator Card

Given an 18 in. by 24 in. simple double-acting engine running 120 rpm under the following conditions:

Cutoff	40 per cent
Clearance	10 " "
Steam-main pressure	130 lb/sq in. abs
Exhaust pressure	2 " " " "
Diagram factor	0.85

Find ihp.

12. Find the steam consumption in pounds per hour and the steam rate (the number of pounds of steam per horsepower hour of work) of the engine of problem 11, on the following assumptions:

Pressure at cutoff	120 lb/sq in. abs
Quality of cutoff	80 per cent
Quality at end of compression	Dry saturation
Pressure at " " "	30 lb/sq in. abs

SYMBOLS

E	internal energy of a system in general
g	acceleration given 1 lb of mass by 1 lb of force (32.174 ft/sec ²)
h	enthalpy per unit mass
m	mass
p	pressure
Q	heat to system
s	entropy per unit mass
u	internal energy of unit system in the absence of motion, gravity, etc.
V	mean velocity
W_r	shaft work delivered by a reversible adiabatic engine
W_x	shaft work delivered by an actual engine

GREEK LETTER

η efficiency of an engine

SUBSCRIPTS

A admission
 c cushion steam
 CO cutoff
 f flow steam
 K compression
 m steam main
 p constant pressure
 R release
 s constant entropy

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CHAPTER XI

THE STEAM TURBINE

The turbine is an engine which derives work from a steady stream of fluid. Its working forces come from changes in the momentum of the fluid stream rather than, as in the reciprocating engine, from the pressure of a static mass. The force exerted by the stream has a component which points in the same direction as the velocity of the part to which it is applied. If it were in the opposite direction work would be absorbed by the machine which might then be a *centrifugal compressor* or a *blower*.

This chapter will serve to illustrate the application of the First and Second Laws to problems in the steady flow of a fluid. A few of the commonest types of turbines will be discussed, but no attempt will be made to describe all the numerous turbinelike devices that have been invented or used.

In general a turbine consists of a series of passages which are formed by pieces of metal called *guides* or *blades*. The stream of fluid passes alternately between guides that are stationary and guides that are moving, or, as in the *Ljungstrom turbine*, alternately between guides that are moving in opposite directions.

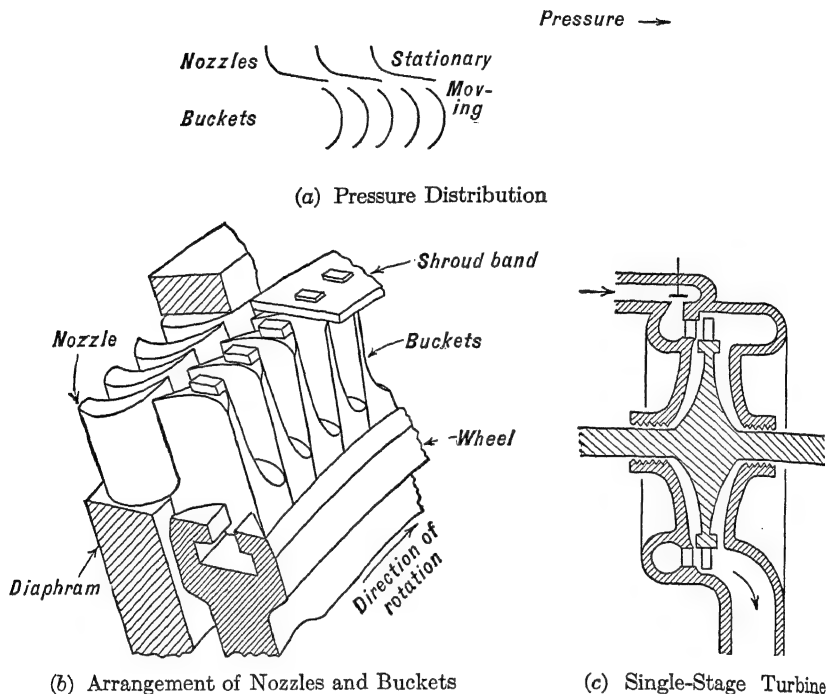
In the stationary passages the stream is given the direction of motion of the next row of moving guides. In the moving passages the velocity of the stream relative to the guides is reversed in direction and sometimes increased in magnitude. The change in direction and velocity results in a force on the moving guides which can be made to do work against external resistances.

Types of Turbines

In each of the three types of turbines described here there is a drop in pressure across the stationary passages or *nozzles* which results in a marked increase in the velocity of the stream. The nozzles direct the stream at the moving vanes which are called *buckets*.

In an *impulse turbine* no change in pressure occurs across the buckets. A *stage* of an impulse turbine usually consists of a row of nozzles followed by a single row of buckets (Fig. 61). Sometimes the single row of nozzles is followed by two moving rows of blades and one intermediate stationary row (Fig. 62). No change in pressure occurs across

any of the three rows following the nozzle. The stationary intermediate passages are not called nozzles because the stream does not



From Newman, *Power Plant Eng'g*, Vol. 41 (1937), p. 538;
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FIG. 61. The Impulse Turbine

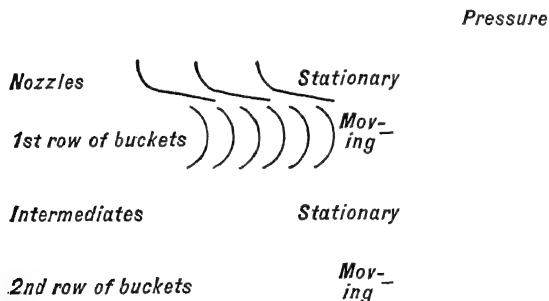


FIG. 62. The Two-Row Impulse Turbine

increase in velocity as it passes through them. This stage is called a *two-row impulse stage*. Occasionally a *three-row stage*, with two rows of intermediate passages, is encountered, but stages with more than

three moving rows are not made today. The two-row and three-row types of stage are called *velocity-compound stages*.

In a *reaction turbine* the pressure falls across the moving blades as well as across the stationary ones (Fig. 63). Usually the drop in pressure across the moving blades is approximately equal to that across the stationary blades. Without this last qualification the term reaction turbine would cover practically all existing types, because there is no way to insure equality of pressure across the moving blades. Moreover, the impulse stage if realized would be merely the limiting case of the reaction stage. Modern multistage turbines are composed of stages in which the drop in pressure across the moving blades ranges from zero to a value slightly in excess of that across the nozzle. Therefore, all multistage turbines are essentially reaction turbines, though the various manufacturers distribute the fall in pressure differently between stationary and moving parts. Turbines of low capacity are likely to approximate closely to the impulse type because small impulse turbines are more efficient than small reaction turbines and cheaper to build.

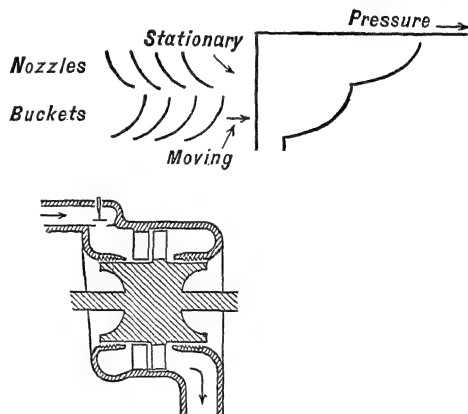


FIG. 63. The Reaction Turbine

The Zero-Angle Turbine

The nozzle of a turbine stage directs the stream of fluid as nearly as is practicable in the same direction as the motion of the buckets. Thus the angle α in Fig. 64 is small.

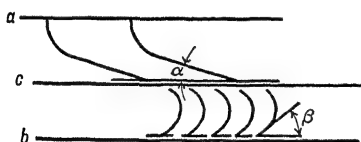


FIG. 64

If it were made vanishingly small the area through which the fluid flows would also be vanishingly small unless the dimension perpendicular to the section of Fig. 64 were indefinitely large. However, we may idealize the nozzle for purposes of analysis and assume its angle to be zero. We may

make a similar assumption concerning the bucket angle β . The results of our analysis will not be strictly applicable to a real stage with finite angles, but they will indicate certain characteristics of a real stage.

We shall assume further that the processes experienced by the fluid

passing through the stage are both reversible and adiabatic: no change in entropy occurs. Then for a given initial state of the fluid the final state is determined by the final pressure, because a second independent property, the entropy, is identical with that of the initial state. Now we may apply the energy equation of steady flow [6] to the stage:

$$h_a + \frac{V_a^2}{2g} = h_b + \frac{V_b^2}{2g} + W_x,$$

where W_x denotes the work delivered to the moving blades per unit mass of fluid entering the stage, subscript a refers to a section preceding the nozzle, and subscript b to a section following the last row of blades. If the inlet velocity is vanishingly small, the last equation simplifies to

$$h_a = h_b + \frac{V_b^2}{2g} + W_x,$$

or

$$W_x = h_a - h_b - \frac{V_b^2}{2g}. \quad [40]$$

If the initial state and final pressure are fixed, the isentropic decrease in enthalpy ($h_a - h_b$) is also fixed. Therefore, the work delivered to the buckets is a maximum when V_b vanishes.

Let us find the velocity vectors for a pure impulse stage. The state of the fluid leaving the nozzle is the same as its state when it leaves the stage, because neither the pressure nor the entropy changes across the bucket. Therefore, the velocity leaving the nozzle, which we shall denote by V_1 , is given by the equation of steady flow

$$h_a = h_b + \frac{V_1^2}{2g},$$

or

$$V_1 = \sqrt{2g(h_a - h_b)},$$

because no work is delivered outside the fluid stream as it passes through the nozzle. We may choose ($h_a - h_b$) to be of such magnitude that V_1 is unity. The speed of the bucket, which we shall call the wheel speed and shall denote by W , is entirely arbitrary. We may select for it a value half as large as V_1 . To an observer moving with the bucket — that is, an observer *standing on* the bucket — the velocity of the stream leaving the nozzle will appear to be less than to a stationary observer by an amount equal to the wheel speed. Velocities seen by an observer standing on the bucket we shall call *relative* velocities, and those seen by an observer standing on the nozzle we shall call *absolute*

velocities. The *relative* velocity entering the bucket, which we shall denote by V_2 , will be $\frac{1}{2}$ for the conditions assumed. To the same observer the velocity leaving the bucket, the relative leaving velocity, is of the same magnitude but reversed in direction. Denoting it by V_3 , we have

$$V_3 = -\frac{1}{2}.$$

We find, then, that the stream leaving the bucket is moving backward relative to the bucket as fast as the bucket is moving forward; so that, to a stationary observer, the velocity of the stream leaving the stage, V_4 , is zero. The vector diagram for this stage is shown in Fig. 65.

The velocity V_4 is identical with the velocity V_b of [40]. The value of V_b^2 will be finite and greater than zero for any value of W other than $\frac{1}{2}$. Therefore, by [40], the work delivered to the buckets is a maximum when

$$\frac{W}{V_1} = \frac{1}{2}. \quad [41]$$

In a reaction stage the relative velocity V_3 leaving the bucket is greater than the relative velocity V_2 entering the bucket by virtue of the pressure drop across the bucket. The state of the fluid leaving the bucket at section b is no longer the same as that of the fluid leaving the nozzle (section c , Fig. 64). The velocity leaving the nozzle is given by

$$V_1 = \sqrt{2g(h_a - h_c)}.$$

The relative velocity leaving the bucket, V_3 , may be found from the energy equation of steady flow as it would be stated by an observer standing on the bucket. He would observe no work between entrance and exit of the bucket, because the bucket is not moving relative to him. Therefore, the energy equation becomes

$$h_c + \frac{V_2^2}{2g} = h_b + \frac{V_3^2}{2g},$$

or

$$V_3 = \sqrt{V_2^2 + 2g(h_c - h_b)}. \quad [42]$$

Let us define a *pure reaction stage* as one in which the isentropic drop in enthalpy across the nozzle is the same as that across the bucket. If the velocity leaving the nozzle is unity and the wheel speed is also unity, then the relative velocity of the fluid approaching the bucket is

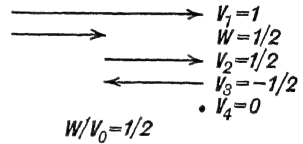


FIG. 65. Impulse Stage

zero. By [42] and the definition just stated, the relative velocity leaving the bucket is unity and the absolute velocity there is zero, as shown in Fig. 66. The work delivered to the buckets is still given by the equation

$$W_x = h_a - h_b - \frac{V_4^2}{2g}, \quad [40]$$

so that the work is a maximum when V_4^2 is zero. For any wheel speed other than unity, V_4^2 is greater than zero. Therefore, the work is a maximum when

$$\frac{W}{V_1} = 1. \quad [43]$$

FIG. 66. Reaction Stage

On comparing [41] and [43] we find that for the same velocity of the nozzle jet the pure reaction stage requires twice as much wheel speed as the pure impulse stage. However, the reaction stage employs a larger drop in enthalpy than does the impulse stage. In order to put the two on a common basis, let us define a velocity V_0 which is a characteristic of the drop in enthalpy across the entire stage: thus

$$V_0 = \sqrt{2g(h_a - h_b)} = \sqrt{2g\Delta h_{ss}},$$

where Δh_{ss} denotes the isentropic drop in enthalpy across the entire stage. Then any two stages, regardless of type, will have identical values of the isentropic drop in enthalpy for identical values of V_0 . For the pure impulse stage discussed above, we get

$$V_0 = V_1,$$

whereas, for the pure reaction stage in which the drop in enthalpy is the same across nozzle and bucket, we have

$$\begin{aligned} V_0 &= \sqrt{2g \ 2 (h_a - h_c)} \\ &= \sqrt{2} V_1. \end{aligned}$$

It follows that for maximum work the ratios of wheel speed to V_0 are as follows:

$$\frac{W}{V_0} = \frac{1}{2} \quad \text{for pure impulse;}$$

$$\frac{W}{V_0} = \frac{1}{\sqrt{2}} \quad \text{for pure reaction.}$$

For the same drop in enthalpy across the stage (the same V_0) the ratio of the wheel speed for pure impulse to that for pure reaction, each corresponding to the wheel speed of maximum work, is $1/\sqrt{2}$.

It is easy to make similar analyses of stages with various other values of the ratio of the drop in enthalpy across the buckets to that across the stage (the enthalpy-drop ratio). The curve of Fig. 67 shows W/V_0 for maximum work for values of the enthalpy-drop ratio less than 1. The abscissa is $\Delta h_{sb}/\Delta h_{ss}$, where Δh_{sb} denotes the isentropic drop in enthalpy across the buckets. Negative values of this ratio denote a rise in enthalpy (and in pressure) across the buckets. When the ratio becomes unity the entire drop in pressure occurs across the bucket and the velocity of the nozzle jet becomes zero. For this case no finite wheel speed will result in a velocity of zero at the bucket exit. Values of the abscissa of Fig. 67 greater than unity will yield imaginary values of W/V_0 , because there is no way by which the drop in enthalpy across the buckets can exceed the drop across the stage if the velocity of the fluid approaching the nozzle is negligible.

Possible values of the ratio $\Delta h_{sb}/\Delta h_{ss}$ range all the way from $+1$ to $-\infty$, but *in practice all values lie between 0 and $\frac{1}{2}$* . Some reasons are given below for the selection of this small range of values.

The value of W/V_0 for maximum work is a measure of the wheel speed required for a given range of expansion. A high value of W/V_0 signifies a large diameter for a given angular velocity or a high angular velocity for a given diameter. In either event the stresses in the rotating parts will be higher for higher W/V_0 and the parts will be correspondingly more expensive. In a multistage turbine a high W/V_0 may signify a low V_0 , which means in turn a small drop in enthalpy per stage and a large number of stages to accommodate the complete drop in pressure. In consequence, the value of W/V_0 may be used as a rough measure of the cost of a turbine, high values of W/V_0 corresponding to high cost and low values to low cost.

From this rule and Fig. 67 one might conclude that a value of $\Delta h_{sb}/\Delta h_{ss}$ approaching $-\infty$ would be desirable. But two other considerations enter, namely, friction and leakage.

Friction forces in turbulent flow vary approximately as the square of

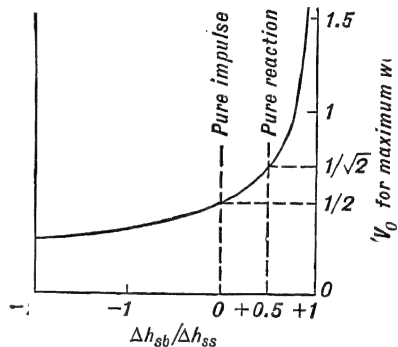


FIG. 67

the velocity; therefore a stage with high stream velocities will suffer serious losses of work from friction. It can readily be shown that for a given V_0 the maximum velocity in a pure reaction stage (which is $1/\sqrt{2}$ times V_0) is lower than the maximum velocity in any other stage if all are operating at the wheel speed of maximum work. Therefore, the pure reaction stage should suffer least from friction.

Fluid that leaks around the buckets through the clearance between moving and stationary parts performs no useful work on the buckets and may gravely affect the efficiency of the stage. The effect becomes greater the larger the drop in pressure across the bucket. For a rise in pressure across the bucket (negative values of $\Delta h_{sb}/\Delta h_{ss}$) the direction of leakage is reversed, but then the effect is even more serious because work must be done on the leakage fluid in bringing it up to the speed of the buckets.* Only in the pure impulse stage is the leakage loss zero.

Because friction favors the reaction stage and leakage the impulse stage, the best turbines will have impulse stages where buckets are short and leakage area is large compared with bucket area, and reaction stages where buckets are long and leakage area is small compared with bucket area. When this rule is followed minor variations in the distribution of impulse and reaction through a multistage turbine seem to have little influence on the efficiency of the turbine.

Efficiency and W/V_0

By selecting various values of W and computing in turn the corresponding vectors V_1 , V_2 , V_3 , and V_4 one may find through [40] the work W_x delivered by each pound of fluid passing through the stage. The efficiency of a turbine stage is defined as

$$\frac{W_x}{\Delta h_s} \quad [44]$$

In terms of the absolute velocity leaving the stage, V_b , we get for the reversible adiabatic stage, by virtue of [40],

$$\eta = 1 - \frac{V_b^2/2g}{\Delta h_{ss}},$$

or, by the definition of V_0 ,

$$\eta = 1 - \left(\frac{V_b}{V_0}\right)^2 \quad [45]$$

Values of this efficiency are given for zero-angle, reversible adiabatic stages of the pure impulse and pure reaction types as functions of

* There is also an interference with the diffusion process in the bucket caused by the slowly moving leakage fluid.

W/V_0 in Fig. 68. The values of the abscissa for maximum efficiency are in accord with Fig. 67.

Both types of stage have an efficiency of zero at a wheel velocity of zero. For a value of W/V_0 of unity the efficiency of the reaction stage is only slightly less than the maximum and that of the impulse stage

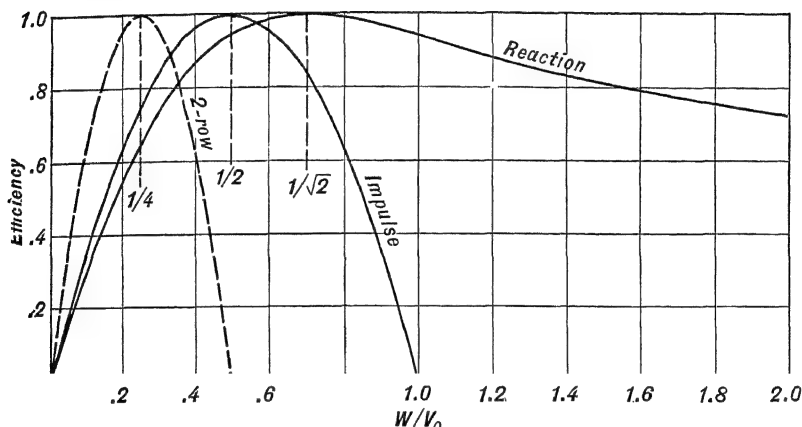


FIG. 68. Variation of Efficiency with W/V_0

has dropped to zero, having passed through its maximum at a value of W/V_0 of $\frac{1}{2}$. As W/V_0 increases beyond unity the efficiency of the reaction stage falls toward $\frac{1}{2}$ as a limit; the efficiency of the impulse stage, for which in this range there is no change in the magnitude or direction of the velocity of the stream after it leaves the nozzle, remains at zero.

The Zero-Angle Two-Row Wheel

The velocity diagram for a two-row stage at the wheel speed of maximum work is shown in Fig. 69. The efficiency of such a stage, which is given by

$$\eta = 1 - \left(\frac{V_8}{V_0} \right)^2 = 1 - \left(\frac{V_8}{V_1} \right)^2$$

is shown by the dash line of Fig. 68 as a function of W/V_0 .

The value of W/V_0 for maximum work is $\frac{1}{4}$ for a two-row stage as compared with $\frac{1}{2}$ for a pure impulse stage and $1/\sqrt{2}$ for a pure reaction stage. For the same drop in enthalpy the two-row stage requires one-half as much wheel speed as a pure impulse stage and only slightly more than one-third as much as a pure reaction stage. Therefore, a

turbine consisting of two-row stages costs less to make than a turbine consisting of single-row stages of either the impulse or the reaction type.

The efficiency of an actual two-row stage is lower, however, than that of either of the other types. For the surfaces on which the steam rubs after it leaves the nozzle are much greater in area than in either of the other types. Moreover, the velocity of the stream relative to the first row of buckets is higher than the velocity relative to the buckets of either of the others, and the friction forces are therefore greater.

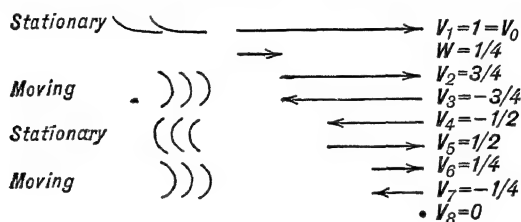


FIG. 69. Two-Row Stage

The two-row stage combines low cost with low efficiency; therefore it is used commonly in turbines of low capacity* or in any turbines for which the cost of the turbine is of more consequence than the cost of the fuel necessary to operation. A relatively efficient type of two-row stage is often used as the first stage in multistage turbines of high capacity and high efficiency. Here its function is to provide a large drop in pressure across the nozzles of the first stage, which its low value of W/V_0 permits, so as to reduce the pressure on the leakage space between the rotor and its casing. This arrangement results in a saving in cost by substituting a two-row stage for several single-row stages, without a corresponding loss in the efficiency of the turbine, because the low efficiency of the two-row stage is compensated by a reduction in leakage loss.

The Reversible Stage with Finite Angles

The velocity diagram for a stage with finite angles is shown in Fig. 70. The absolute velocity leaving the nozzle, V_1 , is denoted by a vector which is inclined at an angle α , the *nozzle angle*, to the plane of rotation of the buckets. The relative velocity approaching the buckets, V_2 , is found by subtracting vectorially the wheel speed, W , from the jet speed, V_1 .

The relative velocity leaving the bucket, V_3 , may be found from [42] as in the zero-angle case:

$$V_3 = \sqrt{V_2^2 + 2g \Delta h_{sb}}, \quad [46]$$

* The *capacity* of a turbine is the amount of power that it can produce.

where Δh_{sb} is the isentropic decrease in enthalpy across the buckets. The absolute velocity leaving the bucket, V_4 , is found by adding vectorially the wheel speed, W , to the relative velocity, V_3 .

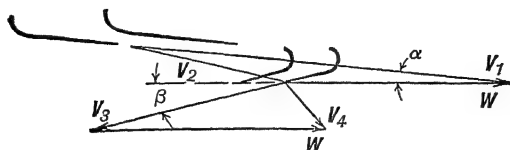


FIG. 70

The work delivered to the buckets per pound of fluid in this reversible case is given by [40] as in the zero-angle case:

$$W_x = \Delta h_{ss} - \frac{V_4^2}{2g}.$$

But, in general, Δh_{ss} is made up of two parts, one the drop in enthalpy across the nozzle, Δh_{sn} , which is equal to the increase in kinetic energy across the nozzle as seen by a stationary observer, and the other the drop in enthalpy across the bucket, Δh_{sb} , which is equal to the increase in kinetic energy across the bucket as seen by an observer on the bucket. Thus

$$\Delta h_{ss} = \frac{V_1^2}{2g} + \left(\frac{V_3^2}{2g} - \frac{V_2^2}{2g} \right).$$

It follows that

$$W_x = \frac{V_1^2 - V_2^2 + V_3^2 - V_4^2}{2g}. \quad [47]$$

It will be shown subsequently that this last equation holds for irreversible stages as well as for reversible ones.

If the efficiency of a finite-angle stage is defined by [44] like that of a zero-angle stage, it becomes for the reversible stage

$$\eta = 1 - \left(\frac{V_4}{V_0} \right)^2$$

as indicated by [45]. Since $(V_4/V_0)^2$ must be always greater than zero, even at the wheel speed of maximum work, the efficiency must be always less than unity. For a given degree of reaction — a given value of $\Delta h_{sb}/\Delta h_{ss}$ — the wheel speed for maximum work will be slightly less than in the corresponding zero-angle stage. Thus, for maximum work the value of W/V_0 will be slightly less than $\frac{1}{2}$ for a pure impulse stage and slightly less than 0.7 for a pure reaction stage.

The Turbine Nozzle

A *nozzle* is a passage which is designed to increase the velocity of a flowing stream. Most turbine nozzles are convergent in the direction of flow, though in a few the convergence is followed by a divergence for reasons that will be given below. All nozzles cause a drop in pressure along the stream, the difference in pressure between the upstream side of a piece of fluid and the downstream side providing the force which accelerates the fluid to higher velocities.

Nozzles of ordinary size have so little wall surface and so much fluid passing through them that transfer of heat between stream and wall per unit mass of fluid is negligible even for appreciable differences in temperature between the two. For this reason the energy equation of steady flow, [6], reduces to

$$h_1 + \frac{V_1^2}{2g} = h_2 + \frac{V_2^2}{2g}$$

for any two sections 1 and 2 through the nozzle passage normal to the direction of flow. If there is an inlet section of very large cross-sectional area as compared with any other section through the nozzle, then the inlet velocity is negligible and we may write

$$h_0 = h + \frac{V^2}{2g}, \quad [48]$$

where subscript 0 refers to the inlet section and symbols without subscript denote mean values of the indicated quantities at any other section through the nozzle. Solving for the mean velocity at the section in question, we get

$$V = \sqrt{2g(h_0 - h)}.$$

The flow through unit area of the cross section is, by [9] (page 38),

$$\frac{w}{a} = \frac{V}{v} = \frac{\sqrt{2g(h_0 - h)}}{v}, \quad [49]$$

where v denotes the mean specific volume of the fluid over the cross section.

The Reversible Adiabatic Nozzle

If friction is negligible, then the flow through the nozzle is reversible as well as adiabatic and the entropy of the fluid is the same at all points in the expansion. Thus, the expansion may be shown on an enthalpy-entropy diagram as a vertical line as in Fig. 71. The point O in Fig. 71 represents the state of the fluid in a very large cross section just before the nozzle passage. The point M represents the state of the fluid at

that section in the nozzle where the pressure is p . In accordance with [6] the height OM is proportional to the kinetic energy at pressure p . The corresponding values of the velocity of the stream for various pressures along the path of the expansion are shown in Fig. 72. In the same figure is shown a curve which gives the value of the specific volume of the vapor at any pressure in the course of the expansion.

The ratio of the velocity of the stream to its specific volume is, by [49], the mass rate of flow per unit area of cross section, which is called more briefly the *flow per unit area* or the *mass velocity*. The flow per unit area is zero at the nozzle inlet where the cross-sectional area is infinite and the velocity is zero. Further along the passage where the pressure is lower the flow per unit area rises to a finite value; but when the pressure falls to zero the flow per unit area also falls to zero, for at this point the velocity in the stream is finite (though large) and the specific volume is infinite. For a value of p/p_0 a little greater than

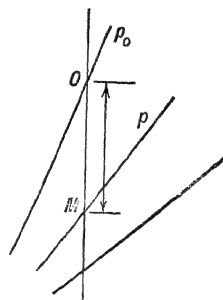


FIG. 71

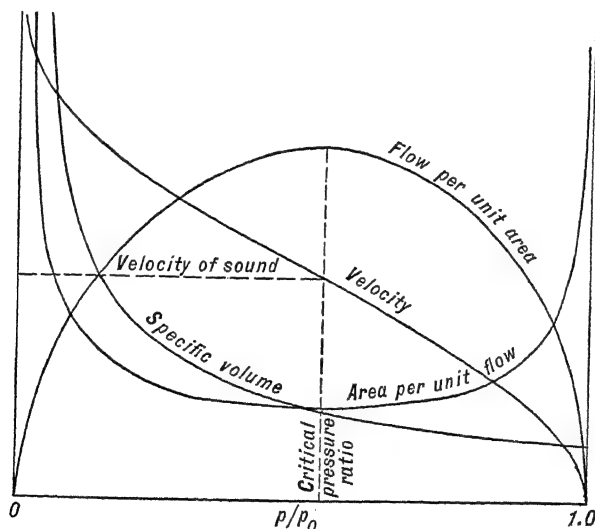


FIG. 72. Characteristics of a Reversible Adiabatic Expansion

$\frac{1}{2}$ the flow per unit area is at its maximum. The pressure ratio at the section of maximum flow per unit area is called the *critical-pressure ratio*.

For steady flow the mass rate of flow is the same past all sections through the nozzle. Therefore, the cross-sectional area of the stream is inversely proportional to the flow per unit area as indicated by the curve of area per unit flow in Fig. 72. Inspection of this curve reveals that for expansion from p_0 down to any pressure short of p_c , the pressure of maximum flow per unit area, the nozzle must be converging; but for expansion to any pressure less than p_c the nozzle must consist of a convergence followed by a divergence. The cross section of minimum area is called the *throat* of the nozzle. It is shown in Chapter XVIII that the velocity of the fluid in the throat of a nozzle is the velocity of sound in that fluid. It follows that velocities in a converging nozzle do not exceed the velocity of sound, while velocities in the diverging part of a nozzle may be considerably in excess of the velocity of sound.

For velocities in excess of the velocity of sound the ratio of the area of a cross section of a stream to its minimum cross-sectional area in reversible adiabatic flow is called the *expansion ratio of the stream* corresponding to the section in question. It may be expressed in either of the following forms:

$$\frac{a}{a_t} = \frac{(w/a)_t}{w/a}$$

or

$$\frac{a}{a_t} = \frac{(V/v)_t}{V/v}$$

where subscript t refers to the throat section and symbols without subscript denote quantities corresponding to a section where the velocity exceeds the velocity of sound.

The *expansion ratio of a nozzle* is the ratio of its cross-sectional area at the exhaust end to its cross-sectional area at the throat. If a stream expands through a nozzle reversibly and adiabatically, filling completely all cross sections of the nozzle, the expansion ratio of the stream in the exhaust section of the nozzle will be identical with the expansion ratio of the nozzle.

The Real Nozzle

Though the flow of a fluid through a real nozzle may be virtually adiabatic it is not reversible because of frictional forces between the fluid and the walls. The degree of departure of the expansion process from reversibility is indicated by the *efficiency of the nozzle*, which is defined as the ratio of the kinetic energy of the stream leaving the nozzle to the kinetic energy of a hypothetical stream leaving a reversible adiabatic nozzle which is supplied with the same kind of fluid in the

same state and at the same velocity and which exhausts to the same pressure as the real nozzle. More briefly, we may write

$$\eta_n = \frac{V_1^2/2g}{(V_a^2/2g) + \Delta h_{sn}} = \frac{V_1^2}{V_a^2 + 2g \Delta h_{sn}} \quad [50]$$

where η_n denotes the efficiency of the nozzle, V_1 the velocity leaving the nozzle, V_a the velocity approaching the nozzle, and Δh_{sn} the isentropic drop in enthalpy from the inlet state to the exhaust pressure.

The *coefficient of velocity* of a nozzle is defined as the ratio of the velocity of the stream leaving the nozzle to the velocity of a hypothetical stream leaving a reversible adiabatic nozzle which is supplied with the same kind of fluid in the same state and at the same velocity and which exhausts to the same pressure as the real nozzle. The coefficient of velocity is the square root of the efficiency; thus

$$c_{vn} = \frac{V_1}{\sqrt{V_a^2 + 2g \Delta h_{sn}}} = \sqrt{\eta_n}, \quad [51]$$

where c_{vn} denotes the coefficient of velocity of the nozzle.

The *coefficient of discharge* of a nozzle for which the ratio of exhaust-chamber pressure to initial pressure is greater than the critical pressure ratio is defined as the ratio of the flow per unit of minimum cross-sectional area to the isentropic flow per unit area corresponding to the actual initial state and initial velocity and the final pressure. Thus,

$$c_w = \frac{wv_s}{a\sqrt{V_a^2 + 2g \Delta h_{sn}}}, \quad [52]$$

where c_w denotes the coefficient of discharge, w the mass rate of flow, v_s the specific volume at the final pressure and the initial entropy, and a the minimum cross-sectional area.

If the ratio of exhaust-chamber pressure to initial pressure is less than the critical pressure ratio the coefficient of discharge is defined as the ratio of the flow per unit of minimum cross-sectional area to the maximum isentropic flow per unit area corresponding to the actual initial state and initial velocity. Thus

$$c_w = \frac{wv_c}{a\sqrt{V_a^2 + 2g \Delta h_c}}$$

where v_c denotes the specific volume at the state fixed by the initial entropy and the critical pressure ratio, and Δh_c the isentropic drop in enthalpy to that state.

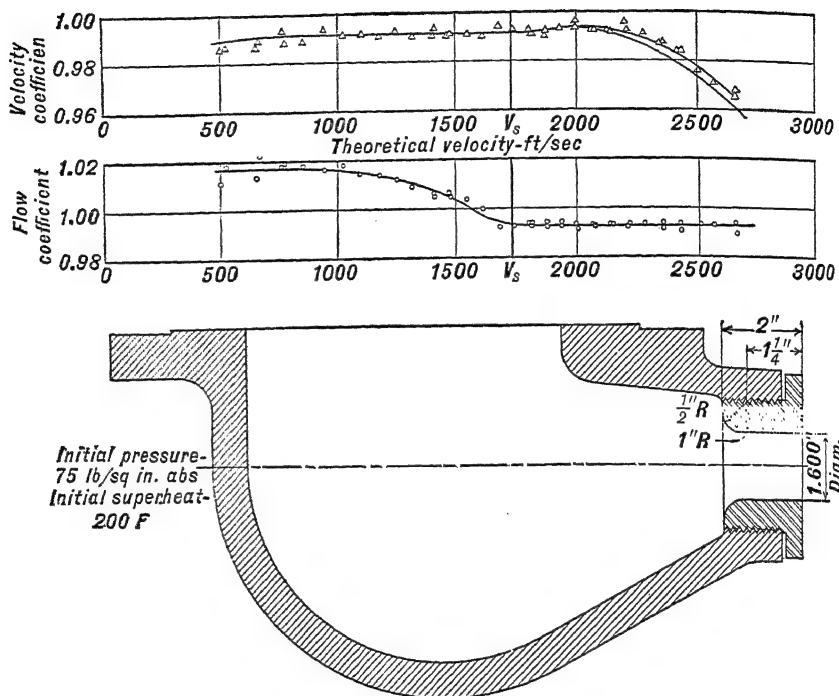


Fig. 73. Results of Tests on a Converging Nozzle

The abscissa is the velocity corresponding to isentropic expansion. The velocity of sound is indicated by V_s . From Warren and Keenan, *Trans. A.S.M.E.*, Vol. 48 (1926), pp. 32-64.

The Converging Nozzle

The coefficient of velocity and the coefficient of discharge for a simple converging nozzle are shown with a longitudinal cross section of the nozzle in Fig. 73. The abscissa is the isentropic velocity corresponding to the conditions of the test. Values of the pressure ratio between unity and the critical pressure ratio correspond to velocities between zero and the velocity of sound; lower pressure ratios correspond to higher velocities. In Fig. 74 the velocity and the discharge are compared with the isentropic velocity and the isentropic discharge, with pressure ratio (the ratio of the pressure in the exhaust chamber to that in the inlet chamber) as abscissa.

It may be seen from Fig. 74 that the discharge from the real nozzle

follows closely the isentropic discharge for pressure ratios greater than the critical pressure ratio. A slight excess of the actual discharge over the isentropic value may be observed, as in this instance, if the pressure in the exhaust section of the nozzle is slightly lower than the pressure in the exhaust chamber. When the pressure ratio is the same as the critical pressure ratio the flow is slightly less than the maximum isentropic flow, the difference between the two being accounted for by friction and by contraction of the stream at the end of the convergence.

Further reduction in pressure ratio causes no increase in flow through the nozzle, because the actual flow cannot exceed the maximum isentropic flow; nor does it cause a decrease in flow as might be expected

from the nature of the curve of isentropic flow per unit area. The characteristics of the curve of actual flow may be explained as follows: The stream of fluid flowing into a gradually converging passage is constrained to convergence within the passage — divergence being accomplished most readily in the exhaust space beyond the end of the nozzle. For pressure ratios higher than the critical pressure ratio the expansion may proceed in a converging stream all the way to the exhaust pressure; but for pressure ratios lower than the critical pressure ratio, expansion to the exhaust pressure involves convergence of the stream followed by divergence. The convergence will occur within the nozzle, but the divergence will occur outside the nozzle in the exhaust space. Therefore, the minimum cross-sectional area of the stream will be the minimum cross-sectional area of the nozzle and will always be the same. For pressure ratios below the critical pressure ratio the flow per unit area at the minimum cross section is fixed by the initial state of the expansion; and it follows that the flow is fixed.

The velocity of the stream leaving a real nozzle is shown by Fig. 74 to follow closely the isentropic velocity for pressure ratios greater than the critical pressure ratio. The actual velocity is always less than the isentropic velocity because of friction, so that the coefficient of velocity, unlike the coefficient of discharge, is always less than unity. It is easy to show that a value greater than unity would result in a decrease in entropy and a violation of the Second Law.

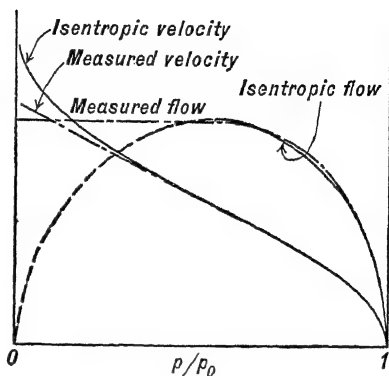


Fig. 74. Curves of Flow and Velocity Corresponding to Fig. 73

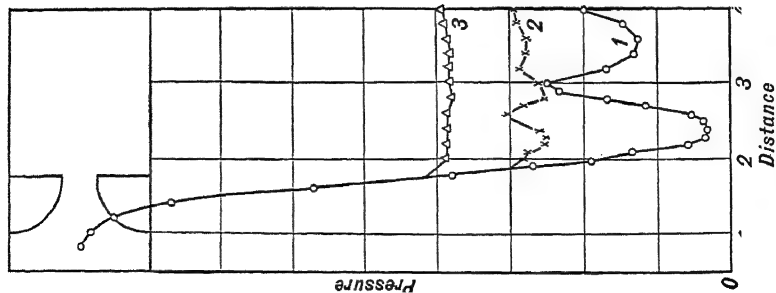


FIG. 75a



FIG. 75b. Corresponding to Curve 2 of FIG. 75a



FIG. 75c. Corresponding to Curve 1 of FIG. 75a

FIG. 75. The Oscillations in Pressure in a Stream from a Converging Nozzle
From Yellott, *Trans. A.S.M.E.*, Vol. 56 (1934), pp. 411-430.

As the pressure ratio is decreased below the critical pressure ratio the actual velocity increases; but it increases less rapidly than the isentropic velocity, and there is a corresponding fall in the velocity coefficient as shown by Fig. 73. The reason for this fall is found in the nature of the "free expansion" outside the nozzle. The lowest pressure within the nozzle passage, as explained above, is the pressure of maximum flow per unit area. Further expansion to the final pressure occurs outside the nozzle. Being entirely unrestrained the expansion is very rapid and the angle of divergence of the boundaries of the stream is large, as shown in Fig. 75. The large transverse components of velocity that are developed cause the stream to diverge to an area greater than that corresponding to the pressure of the exhaust space, and the pressure in the stream therefore falls below the exhaust pressure. The reversal in the pressure difference between the stream and its environment eventually results in a contraction of the stream which is accompanied by an increase in pressure. The result is a series of standing waves of rarefaction and compression which decrease in amplitude with distance beyond the nozzle. The oscillations in pressure experienced by any element of fluid passing through these waves are damped by the action of frictional forces, and the process is therefore irreversible. Consequently, the entropy increases, and the efficiency and coefficient of velocity of the nozzle decrease correspondingly.

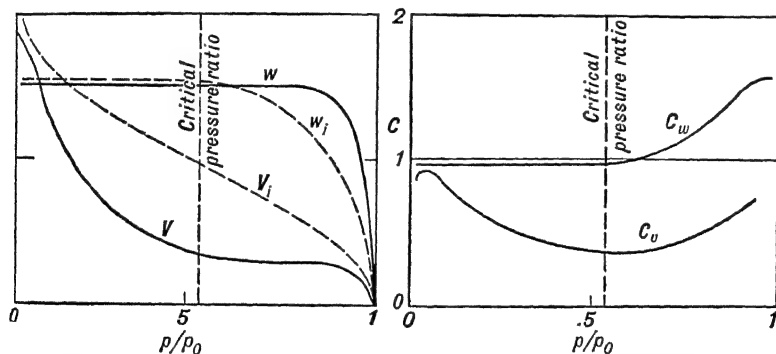


Fig. 76. Characteristic Curves of a Converging-Diverging Nozzle

The Converging-Diverging Nozzle

At velocities well in excess of the velocity of sound a nozzle efficiency greater than that of the converging nozzle can be realized by means of a converging-diverging nozzle. To get the best results the angle between the diverging walls must be small—generally less than

12 degrees. Characteristic curves of flow and velocity for such a nozzle are shown in the charts of Fig. 76.

The mass rate of flow through a converging-diverging nozzle for a given initial state is constant over a larger range of pressure ratios than is that of a converging nozzle. When the pressure ratio is greater than

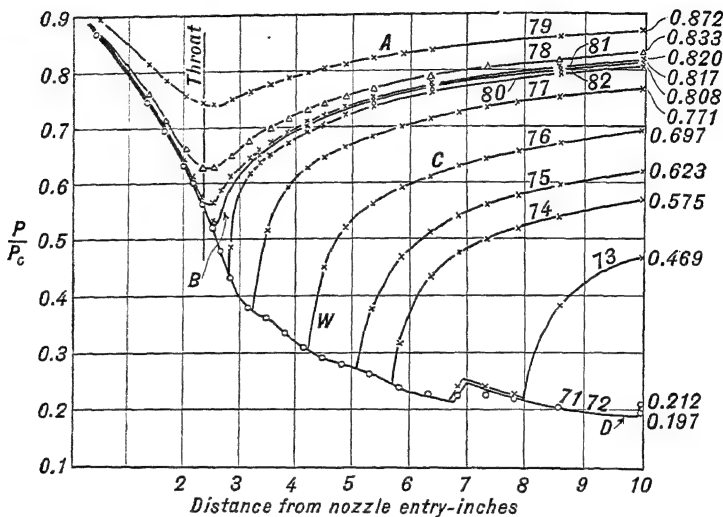


FIG. 77. Pressure Distribution in a Converging-Diverging Nozzle

(The discontinuity in the curve D at 7 inches is a result of condensation.) From Binney and Woods, *Proc. Inst. Mech. Eng.*, Vol. 138 (1938), p. 260.

the critical pressure ratio and the velocity nowhere exceeds the velocity of sound, the diverging part of the nozzle serves as a diffuser and the nozzle as a whole is in every respect like an ordinary venturi tube. The variation in the pressure of the fluid along the length of the stream is shown for this case by curve A of Fig. 77, which shows the minimum pressure occurring in the throat of the nozzle. If the exhaust pressure is lowered the pressure in the throat falls and the flow through the nozzle increases until the ratio of the throat pressure to the initial pressure reaches the critical pressure ratio, as shown by curve B, Fig. 77. No further increase in flow can result from a further decrease in the exhaust pressure because the flow per unit area in the throat of the nozzle has reached its maximum possible value. For all lower exhaust pressures the condition in the throat of the nozzle remains unchanged and the flow remains constant.

The coefficient of discharge for pressure ratios greater than the critical pressure ratio may greatly exceed unity because the isentropic flow, which is used in calculating it, is based on the assumption that the

pressure in the throat of the nozzle is identical with the exhaust pressure. Actually the pressure in the throat, as in the throat of a venturi tube, may be very much lower than the exhaust pressure.

If the exhaust pressure is intermediate between that corresponding to curve *B* of Fig. 77 and that for which the expansion ratios of stream and nozzle are identical, curve *D*, then at some section in the diverging passage there will be a standing pressure wave, shown by *W* on curve *C*, which is called a *pressure shock*. The fluid enters this wave at low pressure and at a velocity exceeding the velocity of sound and leaves it at high pressure at a velocity less than the velocity of sound. At the lower velocity the diverging passage serves as a diffuser and the pressure rises along the rest of the path until it reaches the exhaust pressure at the nozzle exit.

Further discussion of the pressure shock will be reserved for Chapter XVIII. Suffice it to say here that flow through the shock is essentially irreversible and the consequent loss of efficiency reaches a maximum at an exhaust pressure intermediate between the exhaust pressures of

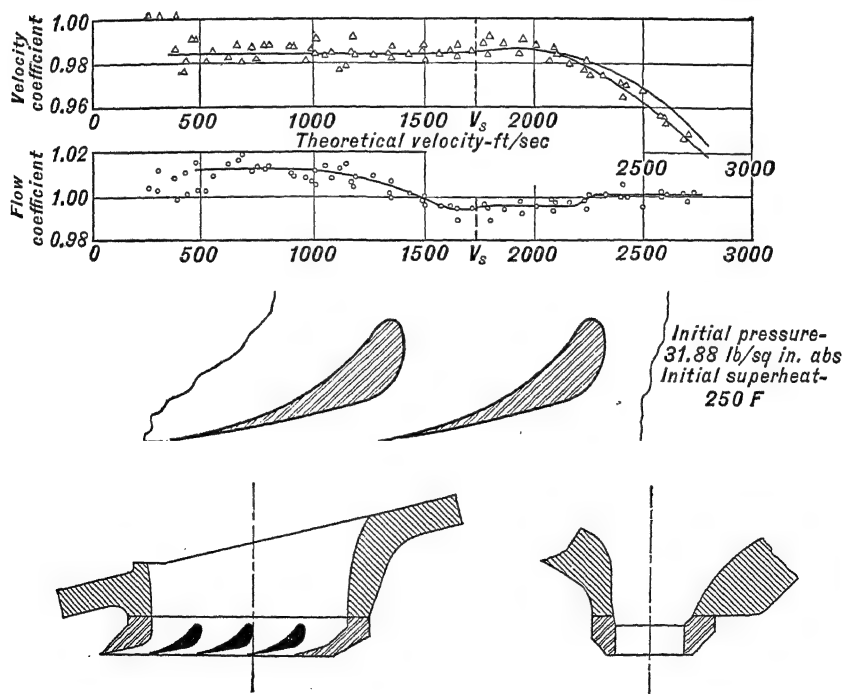


FIG. 78. Results of Tests on a Converging Turbine Nozzle

The abscissa is the velocity corresponding to isentropic expansion. The velocity of sound is indicated by V_s . From Warren and Keenan, *Trans. A.S.M.E.*, Vol. 48 (1926), pp. 32-64.

curves *B* and *D* of Fig. 77. The coefficient of velocity reaches a corresponding minimum as shown by Fig. 76. For exhaust pressures less than that corresponding to curve *D* some free expansion occurs outside the nozzle and causes a decline in the coefficient of velocity at low pressure ratios which is illustrated by Fig. 76.

Characteristics of the Turbine Nozzle

A turbine nozzle must be designed to change the direction as well as the magnitude of the velocity of the fluid stream. In less expensive turbines the nozzle may consist of a hole drilled through a partition with some enlargement of the hole at its upstream end. The angle at which the hole is drilled determines the direction in which the stream will leave the nozzle. A better though more expensive type is shown with its coefficients of velocity and discharge in Fig. 78. The passage is rectangular in cross section, the metal edge, which separates adjacent nozzle streams where they issue from the nozzle, is thin, and the radius of curvature of the convex wall is large compared with the width of the stream.

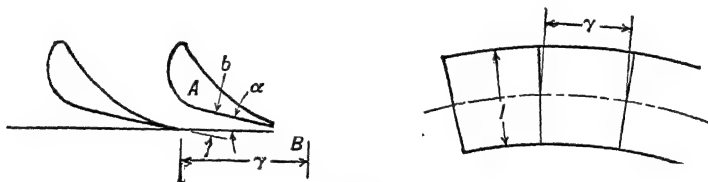


FIG. 79

The *radial height* of a nozzle, l , is its height in the direction of a radius from the center of the shaft; the *pitch*, γ , is the spacing between partitions measured along a circle (the pitch circle) passing through the middle of the nozzle height. In turbines of the impulse type the partition usually has a flat surface, *AB*, Fig. 79, which is inclined at some angle α to the plane of rotation of the wheel. This angle is called the *nozzle angle*, though the angle of the velocity of the stream to the plane of rotation may be slightly different.

The area of the passage normal to the direction of flow at the downstream edge of a partition is called the exit area of the nozzle. In terms of the symbols shown in Fig. 79 it may be written as

$$a = bl,$$

where a denotes the area of a single nozzle. The width b is often expressed in terms of the nozzle angle and the pitch by the equation

$$b = (1 - e)\gamma \sin \alpha,$$

which is in reality a definition of the small quantity e known as the edge factor. The area of a single nozzle is then

$$a = (1 - e)l\gamma \sin \alpha, \quad [53]$$

and the area of a complete ring of such nozzles is

$$\sum a = (1 - e)l\pi D \sin \alpha, \quad [54]$$

where D is the diameter of the pitch circle and is called the *pitch diameter*.

In turbines of the reaction type there is commonly no flat surface on the nozzle partition which may be used to define an angle; instead, the blades or partitions have only curved surfaces as in Fig. 80. The position in which the blades are set is expressed by the *gaging*, j , just as the position of a partition in an impulse turbine is expressed by the nozzle angle. The *gaging* is defined by the expression

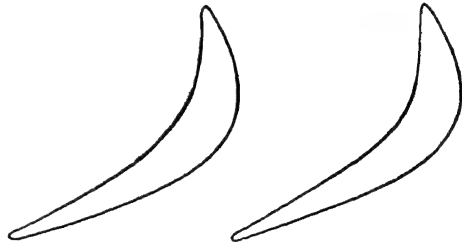


FIG.

$$a = j\gamma l,$$

or by

$$\sum a = j\pi D l. \quad [55]$$

The Turbine Bucket

The passage formed by adjacent buckets on the rotor of a turbine is in general a moving nozzle, the flow in which may be analyzed by an observer standing on the bucket in exactly the same way as the flow in a nozzle may be analyzed by a stationary observer. The bucket passage of an impulse stage is a special case: the case for which the drop in pressure across the moving nozzle is zero.

Bucket passages are almost always converging passages, a diverging portion being desirable only where the relative velocity exceeds appreciably the velocity of sound. Since the relative velocity within the passage is invariably smaller than the velocity at the nozzle exit, this condition is seldom realized.

The degree of reaction in a stage of a turbine is fixed by the relation between the area at the exit of the nozzle and that at the exit of the bucket. If the exit area of the bucket passage is made small enough a pressure difference will be built up across the bucket by the stream. For this reason the graphic term *choke* is sometimes used to denote reaction or drop in pressure across the bucket.

Because the bucket passage is essentially a nozzle we may carry over to it the definitions of efficiency, coefficient of velocity, and coefficient of discharge given by [50], [51], and [52], respectively. To an observer on the bucket these become

$$\eta_b = \frac{V_3^2}{V_2^2 + 2g \Delta h_{sb}}$$

$$c_{vb} = \frac{V_3}{\sqrt{V_2^2 + 2g \Delta h_{sb}}}$$

$$= \sqrt{\eta_b}$$

and

$$c_{wb} = \frac{wv_s}{a\sqrt{V_2^2 + 2g \Delta h_{sb}}},$$

where Δh_{sb} denotes the isentropic drop in enthalpy across the bucket, a the exit area of the bucket passage, v_s the specific volume at a state corresponding to the pressure after the bucket and the entropy before the bucket, and V_2 and V_3 the relative velocities respectively at entrance and exit of the bucket. For pure impulse these reduce to

$$\eta_b = \left(\frac{V_3}{V_2}\right)^2 = c_{vb}^2$$

and

$$c_{wb} = \frac{wv_s}{aV_2},$$

where v_s is now the specific volume of the fluid entering the bucket passage.

The Force on the Bucket

To determine the force applied to a turbine bucket we must employ Newton's Second Law of Motion, which may be written for any system of mass m

$$F = \frac{ma}{g}, \quad [56]$$

where F denotes the resultant force applied to the system, a the acceleration of the system in the direction of F , and g^* the acceleration

* If F is expressed in pounds of force and m in pounds of mass, then g is the *standard acceleration of gravity*, namely, 32.174 ft/sec². This is common practice in engineering. In the science of physics, on the other hand, the units of force and mass are so chosen as to make g equal to unity in the equation above.

given to unit mass by unit force. If a number of forces of different magnitudes and directions are applied to a system, the resultant force may be found by a vector summation of the forces which may be illustrated by the *funicular polygon* of Fig. 81, in which F_1 , F_2 , and F_3 are individual forces and F is their resultant. In the language of vector analysis the summation is written

$$\mathbf{F} = \mathbf{F}_1 + \mathbf{F}_2 + \mathbf{F}_3,$$

where bold-face type signifies vector quantities.

Let us apply the Second Law of Motion to a particle of fluid which is part of a steady stream flowing in a curved path. Consider the elementary mass (Fig. 82) bounded by the parallel planes aa' and bb' and by the surfaces ab and $a'b'$ which are in the directions of the local velocities.

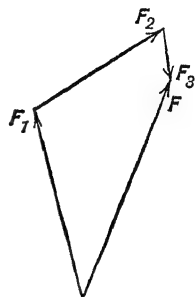


FIG. 81

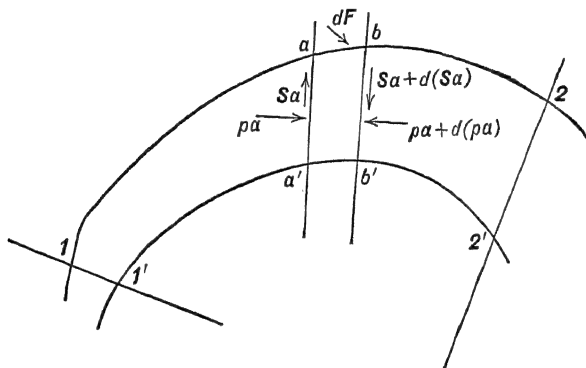


FIG. 82

The forces acting on the element may be listed as follows:

1. Normal forces applied at sections aa' and bb' by fluid respectively following and leading the element.
2. Shearing forces applied at sections aa' and bb' by fluid respectively following and leading the element.
3. Forces applied at boundaries ab and $a'b'$ by fluid outside these boundaries.

We may denote the normal force at aa' by the vector \mathbf{pa} and that at bb' by the vector $\mathbf{pa} + d(\mathbf{pa})$, which is opposed in direction to \mathbf{pa} . Thus, the net normal force acting on the two ends is a vector $-d(\mathbf{pa})$. Similarly, the net shearing force acting on the two ends is the vector $-d(\mathbf{Sa})$, where

S denotes the shear stress intensity. The net force on the element is given by the vector summation

$$d\mathbf{F} - d(\mathbf{pa}) - d(\mathbf{Sa}),$$

where $d\mathbf{F}$ denotes the force applied by fluid outside the boundaries ab and $a'b'$. The Second Law of Motion as applied to this element becomes

$$d\mathbf{F} - d(\mathbf{pa}) - d(\mathbf{Sa}) = \frac{dm}{a} \frac{d\mathbf{V}}{dt} \quad [57]$$

where the vector \mathbf{V} denotes the velocity of the element. If the time dt is chosen to be the time required for the element to cross the boundary bb' , then dm/dt is the mass rate of flow and $d\mathbf{V}$ is the change in the velocity vector between the present time and the time when the element occupies its next adjacent position. The element which we have studied is merely a piece of a stream tube or filament whose boundaries $1ab2$ and $1'a'b'2'$ (Fig. 82) are everywhere in the direction of flow. If this tube is split up into an infinite number of such elements between section $11'$ and $22'$ the summation of the terms of [57] for all of them becomes

$$\mathbf{F} + (\mathbf{pa})_1 - (\mathbf{pa})_2 + (\mathbf{Sa})_1 - (\mathbf{Sa})_2 = \frac{w}{g} (\mathbf{V}_2 - \mathbf{V}_1) \quad [58]$$

where w denotes the mass rate of flow through the filament and subscripts 1 and 2 refer to sections $11'$ and $22'$ respectively. It has been assumed that a_1 and a_2 are so small that the velocity is uniform across each of them except for infinitesimal variations. For finite values of a_1 and a_2 integration changes only* the expression for the right-hand side of [58], making it

$$\left. \int_{a=0}^{a=a_2} G_2 \mathbf{V}_2 da - \int_{a=0}^{a=a_1} G_1 \mathbf{V}_1 da \right\},$$

where G denotes the mass flow per unit area. Otherwise, [58] may be left in its present form with the understanding that \mathbf{V} denotes a mean velocity over the section.

If sections $11'$ and $22'$ are each placed in a region where the velocity is uniform, then there can be no shearing stresses applied by leading and following fluid and [58] simplifies to

$$\mathbf{F} + (\mathbf{pa})_1 - (\mathbf{pa})_2 = \frac{w}{g} (\mathbf{V}_2 - \mathbf{V}_1). \quad [59]$$

* It is shown in Chapter XVIII that the summation of the values of \mathbf{F} for a bundle of stream tubes is the force applied to the bundle by the surrounding fluid or walls.

(The same result would follow if the values of S were both positive and negative over each section and were so distributed that \mathbf{Sa} would vanish.) This is an expression of great utility. It may be taken out of the vector form and expressed in terms of components, for instance, in the direction x :

$$F_x + (pa)_{1x} - (pa)_{2x} = \frac{w}{g} (V_{2x} - V_{1x}). \quad [60]$$

When we apply it to the stream flowing through a bucket passage of a turbine the force \mathbf{F} becomes the force applied to the stream by the buckets which are now the boundaries of the stream; and F_x becomes the component of that force in the direction x . If the direction x is in the plane of the turbine wheel and tangent to the pitch circle at the passage in question it is called the *tangential* direction and the corresponding components are called tangential components. The tangential components of $(\mathbf{pa})_1$ and $(\mathbf{pa})_2$ vanish, so that [60] becomes

$$F'_t = \frac{w}{g} (u_b - u_a), \quad [61]$$

where F'_t denotes the tangential component of the force applied by the buckets on the stream and u_b and u_a are respectively the tangential components of the leaving and entering velocities.

In studies of the turbine we are interested in the force applied by the stream on the buckets, which by Newton's Third Law is equal in magnitude to the force applied by the buckets on the stream but opposite in direction. Denoting the tangential component of the force on the buckets by F_t , we get

$$F_t = \frac{w}{g} (u_a - u_b). \quad [62]$$

Since the Newtonian equation [56] is true regardless of the velocity of the observer, it follows that [62] may be expressed in terms of either absolute or relative velocities. Thus, in terms of the tangential components u_1 and u_4 (Fig. 83) of the absolute velocities V_1 and V_4 , [62] becomes

$$F_t = \frac{w}{g} (u_1 - u_4), \quad [63]$$

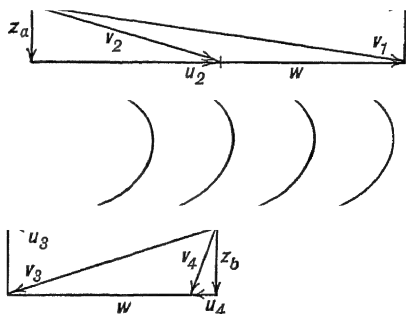


FIG. 83

and in terms of the tangential components u_2 and u_3 of the relative velocities V_2 and V_3 ,

$$F_t = \frac{w}{g} (u_2 - u_3). \quad [64]$$

The component of the force on the buckets in the direction of the axis of rotation, which is called the *axial thrust*, may also be deduced

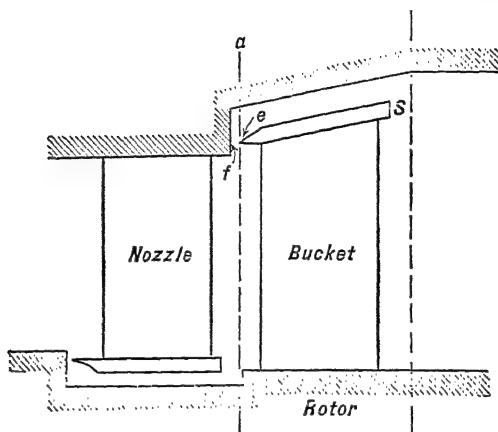


FIG. 84

from [60]. Let us find, for example, an expression for the axial thrust on the bucket shown in Fig. 84. The axial component of the force applied by the bucket to the stream is, by [60],

$$F'_a = \frac{w}{g} (z_b - z_a) + (pa)_b - (pa)_a, \quad [65]$$

where F'_a denotes the axial component of the force, z the axial component of the velocity, and subscripts a and b refer respectively to the sections immediately before and after the bucket. The area a_a is the inlet annulus area of the ring of buckets, and the area a_b is the outlet annulus area. To get the total axial thrust on any part of a turbine rotor the axial components of all normal forces applied to surfaces not directly exposed to the fluid stream must be summed up along with the axial thrust of the stream, which is $-F'_a$. For example, denoting the axial thrust to the right on the bucket and its shroud band S of Fig. 84 by A , we may write

$$A = \frac{w}{g} (z_a - z_b) + (pa)_a - (pa)_b + p_b(a_b - a_a). \quad [66]$$

Here $p_b(a_b - a_a)$ is the net thrust applied to the shroud band by fluid

outside the bucket passage, because the pressure p_b will be exerted on the outside of the shroud band if the sharp front edge e of the band runs sufficiently close to the stationary surface f . The expression [66] simplifies to

$$A = \frac{w}{g} (z_a - z_b) + a_a(p_a - p_b).$$

Work on the Turbine Bucket

The work done by the stream on the buckets is the product of the tangential component of the force applied to the buckets, as given by [62], and the distance moved by the buckets. For unit time this product is

$$\frac{w}{g} (u_a - u_b)W, \quad [67]$$

where W is the velocity of the bucket. The work done on the buckets per pound of fluid entering the stage, which we shall denote by W_x , is found by dividing [67] by w ; thus

$$W_x = \frac{W}{g} (u_a - u_b). \quad [68]$$

In order to find another expression for the work W_x we shall employ the fact that the subscripts a and b of [68] may be interpreted either as 1 and 4 or as 2 and 3. Thus, we may write

$$W_x = \frac{1}{2} \frac{W}{g} [(u_1 - u_4) + (u_2 - u_3)]. \quad [69]$$

Moreover, the tangential component of the relative velocity of the given stream is less by an amount equal to the wheel speed than the tangential component of its absolute velocity; that is,

$$W = u_1 - u_2$$

and

$$W = u_4 - u_3.$$

Therefore, [69] may be written

$$W_x = \frac{1}{2g} [(u_1 - u_2)(u_1 + u_2) - (u_4 + u_3)(u_4 - u_3)]$$

or

$$W_x = \frac{1}{2g} (u_1^2 - u_2^2 + u_3^2 - u_4^2). \quad [70]$$

This last equation may be expressed in terms of the resultant velocities instead of their tangential components if we note first that the axial

components of the relative and absolute velocities of a given stream are identical, and second that the square of a resultant velocity is the sum of the squares of its axial and tangential components. Thus we get

$$W_x = \frac{1}{2g} (V_1^2 - V_2^2 + V_3^2 - V_4^2). \quad [47]$$

This equation, which is here shown to be of general application, was shown on page 135 to hold for the reversible adiabatic case. Equations [47] and [68] are entirely equivalent. The one to be used in any instance is determined by convenience.

The work on a turbine bucket may also be found through an energy analysis. Let us write the energy equation of steady flow, first from the standpoint of a stationary observer, and second from the standpoint of an observer on the bucket. The first observer sees that work is being done on the buckets between section *a* before the bucket and section *b* after it, so that his equation becomes

$$h_a + \frac{V_1^2}{2g} = h_b + \frac{V_4^2}{2g} + W_x.$$

The second observer sees no work being done because the boundaries of the stream do not move relative to him, and his equation becomes

$$h_a + \frac{V_2^2}{2g} = h_b + \frac{V_3^2}{2g}.$$

Subtracting the second from the first and solving for W_x , we get

$$W_x = \frac{1}{2g} (V_1^2 - V_2^2 + V_3^2 - V_4^2),$$

which is identical with [47]. By reversing the analytical steps of the preceding paragraphs we arrive again at the expression for the tangential component of the force on the buckets, this time without explicit reference to the Newtonian Laws of Motion. Reference is implicit, however, in that the energy equation of steady flow, as it is stated above, includes terms which arise from introduction of the Newtonian Laws into the expression for internal energy, as explained on pages 31 and 32.

The Turbine Stage

For the purposes of our discussion a *stage* in a multistage turbine will be considered that part of a turbine between two planes perpendicular

to the axis of rotation which are respectively at the inlet ends of two successive rings of nozzles. (A nozzle is defined in turn as a stationary passage in which the stream accelerates appreciably.)

The characteristic velocity of a turbine stage, V_0 , is defined by the relation

$$\frac{V_0^2}{2g} = \frac{V_a^2}{2g} + \Delta h_{ss}, \quad [71]$$

where V_a denotes the velocity approaching the nozzles of the stage and Δh_{ss} the isentropic drop in enthalpy from the initial state of the fluid to the final pressure in the stage.

The definition of the efficiency of a turbine stage is aimed at a comparison of the performance of the actual stage with that of a reversible adiabatic stage. In the latter the entropy is constant, and we may denote the drop in enthalpy across the stage by Δh_{ss} . The work delivered by each pound of steam as it passes through a reversible adiabatic stage is given, in accordance with [6], by the expression

$$\frac{V_a^2}{2g} + \Delta h_{ss} - \frac{V_b^2}{2g},$$

where V_a and V_b denote respectively the velocities at entrance and exit. In a carefully designed turbine V_a and V_b will be nearly identical. For this reason and for reasons of convenience the quantity Δh_{ss} is usually chosen, instead of the longer expression given above, as the basis of comparison in defining the efficiency of a stage. Thus the efficiency becomes the ratio of the work per pound of steam to the isentropic drop in enthalpy between the state of the steam at the entrance to the actual stage and the pressure at the exit from the stage. There may be at least two such efficiencies because the work which appears in the numerator may be the work done on the buckets or the work delivered to the shaft of the turbine.

The ratio of the work done on the buckets of a stage to the isentropic drop in enthalpy is called the nozzle-bucket efficiency and is denoted by η_{nb} :

$$\eta_{nb} = \frac{W_x}{\Delta h_{ss}},$$

where W_x denotes the work on the buckets per unit mass of fluid entering the stage. The nozzle-bucket efficiency is shown in Fig. 85 as a function of the wheel-speed ratio W/V_0 for typical examples of impulse, reaction, and two-row stages. Some reasons for the characteristics of the curves of Fig. 85 were given on page 132.

The *stage efficiency* is the quotient of the work delivered to the shaft of the turbine per unit mass of fluid entering the stage divided by the isentropic drop in enthalpy. Not all the work done by the stream on

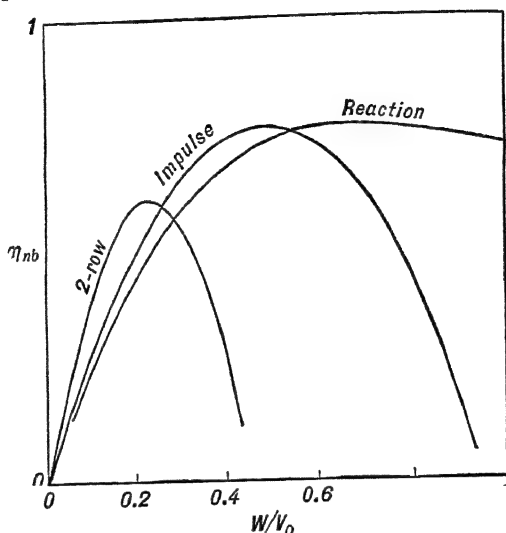


FIG. 85

the turbine buckets reaches the turbine shaft, because some is consumed in maintaining the motion of parts of the stage which are in contact with fluid other than that in the main stream. Thus, if the stage includes a rotating disk, some work is consumed in keeping the disk moving through the surrounding fluid; and if some of the buckets are not fed by a nozzle jet, some work is consumed in keeping these buckets moving. The work so consumed is called the *rotation loss* of the stage. Now we may express the stage efficiency in the form

$$\eta_s = \frac{W_x - L}{\Delta h_{ss}}$$

$$= \eta_{nb} - \frac{L}{\Delta h_s}$$

where η_s denotes the stage efficiency, W_x the work done by the stream on the buckets per unit mass of fluid, and L the rotation loss per unit mass of fluid.

Rotation Loss

It is well known that for turbulent motion of a fluid past an unpolished surface the frictional resistance to the motion of the fluid follows

closely the relation

$$R = \ell \rho V^2, \quad [72]$$

where R denotes the frictional force per unit area of surface, ρ the mass density of the fluid which is otherwise $1/vg$, V the velocity of the fluid relative to the surface, and ℓ a constant. Let us apply this relation to the motion of a rotating disk in a fluid atmosphere.

Consider an annular area on the surface of the disk (Fig. 86) at a radius r from the center of rotation and of width dr . The frictional torque applied to this annulus is then

$$dT = R 2\pi r^2 dr.$$

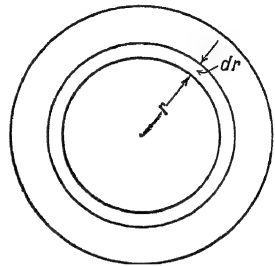


FIG. 86

Substituting the right-hand member of [72] for R and expressing the velocity of the annulus (the relative velocity of the fluid) in terms of the angular velocity of the disk, ω , we get

$$dT = 2\pi \ell \rho \omega^2 r^4 dr.$$

Integrating between the shaft radius r' and the disk radius r , we get for the torque

$$T = \frac{c_d \omega^2 (r^5 - r'^5)}{v},$$

where c_d denotes a constant and v the specific volume of the fluid. Except in unusual cases the fifth power of the shaft radius will be negligible as compared with the fifth power of the disk radius, so that the expression for the torque is simply

$$T = c_d \omega^2 r^5$$

The power consumed in moving the disk is therefore given by an expression of the form

$$P_d = T\omega = \frac{c_d \omega^3 r^5}{v}.$$

We may assume that a rule similar to [72] holds for resistance to the motion of a row of idle buckets through a fluid. The corresponding torque may be written for a relatively short bucket.

$$T_b = \frac{c_b x \omega^2 r^4 l}{..},$$

where c_b denotes a constant, x the fraction of the periphery over which the buckets are idle and l the length of the buckets. Then the power consumed in moving the idle buckets is given by

$$P_b = \frac{c_b x \omega^3 r^4 l}{v}.$$

If the radius to the pitch circle may be considered to approximate the radius of the disk, then the total rotation loss per unit time for disk and idle buckets is given by the sum

$$P = P_d + P_b = \frac{c_1 \omega^3 r^5}{v} \left(1 + \frac{c_2 l}{r} \right)$$

where c_1 and c_2 denote constants which must be determined by experiment. Stodola* gives a formula similar to this, except that l appears to the 1.5 power instead of to the first power, with experimentally determined coefficients. It is as follows:

$$P = 0.027 \left(\frac{W}{100} \right)^3 \frac{D^2}{v} \left(1 + \frac{15l^{1.5}}{D} \right) \quad [73]$$

where P denotes the rotation loss in kilowatts, l the radial height of the buckets in inches, D the pitch diameter of the stage in feet, W the wheel speed at the pitch circle in feet per second, and v the specific volume of the surrounding fluid in cubic feet per pound.

The Multistage Turbine

Steam turbines are made with stages ranging in number from one to about a hundred. Those with more than two or three stages are commonly called *multistage* turbines. In general, the greater the number of stages, the more efficient is the turbine, other things being the same. Therefore, the single-stage type is used only where operating costs are small compared with fixed costs.

Certain practical difficulties face the designer of a single-stage turbine which is to receive steam at a high pressure and exhaust it at a low one. For example, consider the design of a single-stage turbine which is to receive steam at 200 lb/sq in. abs and 700 F and exhaust it to a condenser at 2 in. Hg abs. The isentropic drop in enthalpy is 412 Btu/lb, and the characteristic velocity V_0 is 4750 ft/sec. For an impulse type of turbine the wheel speed for maximum efficiency will be slightly less than half of 4750 ft/sec, or, say, 2300 ft/sec. The stress in a disk of

* *Steam and Gas Turbines*, Stodola-Lowenstein, McGraw-Hill (1927), p. 200.

uniform thickness with a peripheral speed of 2300 ft/sec is about 240,000 lb/sq in. — an impossible figure for ordinary materials. It can be reduced by shaping the disk properly, but cannot by any practical device be brought within a safe limit for the usual metals. The speed of a reaction turbine wheel for maximum efficiency would be about 3000 ft/sec, and the stress in a disk of uniform thickness would be about 400,000 lb/sq in., which is still further from the range of practice. On the other hand, the two-row impulse wheel at 1100 ft/sec and a stress of 55,000 lb/sq in. is near to the practicable and might be employed with a modified design of the disk. There will be, however, a marked loss in efficiency as compared with the single-row turbine of either the reaction or impulse type.

This example serves to illustrate why the multistage turbine is preferred to the single-stage. Some other reasons are as follows: First, certain friction losses of some consequence are associated with the radial extremes of the nozzle and bucket passages. By subdividing the expansion and, consequently, reducing the wheel diameters, the designer can make the radial heights of the passages greater and thereby increase the ratio of the radial height to the width of the stream. The end effects are thereby reduced. Second, in many instances the smaller diameter of the multistage turbine for a given angular velocity permits the distribution of nozzles around the whole pitch circle, whereas the same nozzle area in a single-stage turbine would be spread over a small arc in order to maintain a radial height of ordinary magnitude. The full peripheral admission of the multistage turbine eliminates serious rotation losses attributable to idle buckets. Third, the stream velocities in any one stage of a multistage turbine being smaller than those in a single-stage turbine, the kinetic energy leaving the last stage of the multistage turbine will be less than that leaving the single-stage turbine. The leaving kinetic energy is called the *leaving loss* because it represents possible work that is not realized. The multistage turbine has less leaving loss than a single-stage turbine.

Some other advantages of the multistage turbine will appear in subsequent paragraphs. The most obvious disadvantage is the relatively high cost of a turbine comprising a large number of stages. Another and less important disadvantage follows from the fact that the pressure of the fluid on the clearance space between shaft and casing, being the same as the pressure after the first row of nozzles, is much higher in a multistage turbine than in a single-stage turbine, and the leakage loss is therefore higher. A two-row stage is often used as the first stage of a multistage turbine to permit a large drop in pressure across the first-stage nozzle and to reduce in turn the pressure on the leakage space.

Multistage Turbine Types

A multistage turbine of the impulse type consists of a series of disks mounted on a shaft and carrying on their periphery the buckets of the stages, and a surrounding casing in which are stationary diaphragms

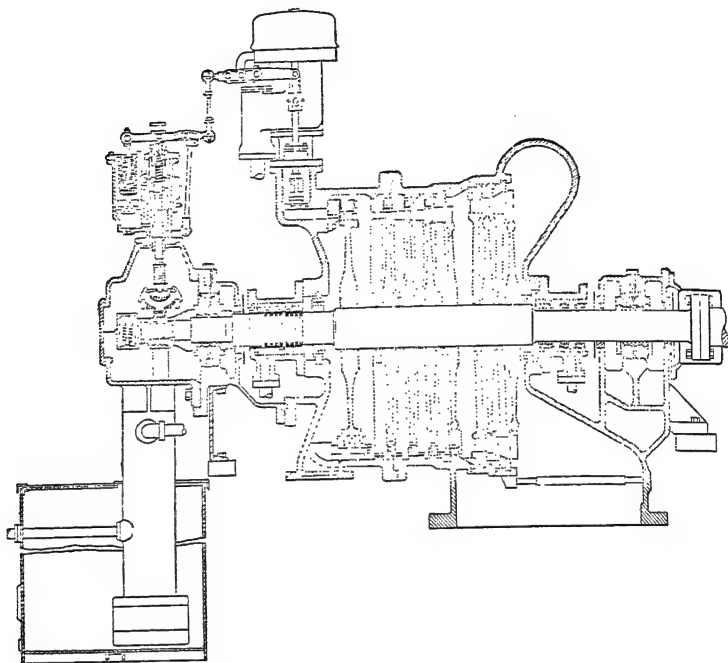


FIG. 87. Impulse Turbine by General Electric Company

From Newman, *Power Plant Eng'g*, Vol. 41 (1937), p. 538, by permission of the General Electric Company.

that extend radially inward between the disks (Fig. 87). The nozzle passages pierce the diaphragms. The inner edges of the diaphragms are made to fit as closely to the revolving shaft as is practicable, because the smaller the clearance between the two parts the less will be the amount of fluid that leaks from stage to stage without passing through the nozzles and, therefore, without doing work on the buckets. Leakage around the buckets and disks is not of serious consequence because virtually all change in pressure in the stage occurs across the nozzle. Indeed, it is common practice to drill holes through the disks to relieve any difference in pressure that might otherwise develop and thereby to eliminate axial thrust on the disk.

The disk type of construction is not employed in the multistage reaction turbine because the pressure difference across each row of

buckets is large and would result in excessive axial thrust on disks. Therefore, the reaction turbine rotor is generally a drum (Fig. 88) on which the rows of buckets are mounted. The outer ends of the nozzle partitions are fastened to the casing; the inner ends are brought as near to the surface of the revolving drum as practicable in order to reduce leakage between the stationary and rotating parts. The inner ends of the buckets are fastened to the drum, and the other ends are brought as near to the inside surface of the casing as practicable.

The drum is extended at the high-pressure end beyond the rows of buckets, and the casing is brought close enough to it at *A* to seal the fluid space from another space *B* into which the end of the drum pro-

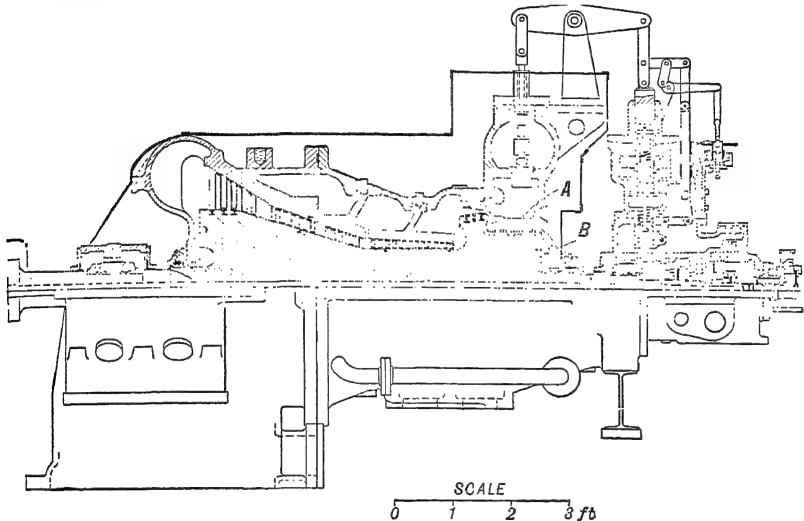


Fig. 88. Reaction Turbine by Westinghouse — 5000 kw, 3600 rpm, 390 lb/sq in. g, 750 F, 28 in. Hg vacuum

By permission of the Westinghouse Electric and Manufacturing Company.

jects. This second space is in turn sealed from the atmosphere. The pressure within it may be adjusted, by means of equalizing pipes, so that it is the same as that on the other end of the drum; or it may be made such as to cause a thrust of any desired magnitude in either direction. When the turbine is designed the diameter of the drum at the high-pressure seal is selected with this object in view.

The Condition Curve

All the states assumed by the fluid in various stages of a reversible, adiabatic, and multistage turbine would be states of identical entropy, however they might differ in pressure and temperature. In a real

is represented by point a in Fig. 89, which is the intersection of the line of pressure p_a and the condition curve. If the stage were reversible and adiabatic it would deliver work corresponding to the height ad along the line of constant entropy between state a and pressure p_d , provided that inlet and exhaust velocities were equal. On the other hand, a stage which is part of a reversible adiabatic turbine and which operates between the same two pressures would deliver work corresponding to the height $a'd'$ between the pressure lines p_a and p_d along a line of constant entropy passing through the point corresponding to the state of the fluid approaching the first stage of the turbine. Now for all known vapors the lines of constant pressure diverge with increasing entropy,* so that the height ad is greater than the height $a'd'$. Therefore, the limiting value of the work for an adiabatic stage is increased by virtue of the inefficiency of the preceding stages.

If the stages of a turbine all have the same efficiency, η_s , then the total work delivered by the fluid in all the stages may be expressed as

$$W_t = \sum W_s = \eta_s \sum \Delta h_{ss}, \quad [75]$$

where W_t denotes the work done by each unit mass of fluid as it flows through the turbine, W_s the work it does as it flows through a stage, and Δh_{ss} the isentropic enthalpy drop for a stage, corresponding to height ad in Fig. 89.

Now let us define a turbine efficiency as the ratio of the work done by the fluid on the rotor of the turbine to the work the fluid would do in a reversible adiabatic turbine operating between the same initial state of the fluid and the same final pressure as in the real turbine: thus,

$$\eta_t = \frac{W_t}{\Delta h_{st}} \quad [76]$$

where η_t denotes the turbine efficiency and Δh_{st} the isentropic drop in enthalpy for the entire turbine as shown in Fig. 89. We may compare this expression with the corresponding expression for constant stage efficiency as obtained from [75]:

$$\eta_s = \frac{W_t}{\sum \Delta h_{ss}}. \quad [77]$$

* Since $ds = (du + p dv)/T = (dh - v dp)/T$, then for constant entropy $dh = v dp$ and $(\partial h/\partial p)_s = v$. If v increases with entropy at constant pressure, that is, if $(\partial v/\partial s)_p$ is greater than zero, then $(\partial h/\partial p)_s$ also increases and the isentropic drop in enthalpy between two pressures will increase with increasing entropy. It is shown in Chapter XXIV that, for any substance which increases in temperature with isentropic compression, $(\partial v/\partial s)_p > 0$. The vapor phases of all known substance have this characteristic. Liquid water below 4°C has the reverse characteristic and would, therefore, have reheat factors less than unity.

It was pointed out above that $\sum \Delta h_{ss}$ exceeds Δh_{st} . Therefore, the efficiency of the turbine, η_t , exceeds the uniform efficiency of the stages which constitute the turbine.

The ratio of the summation of all the isentropic decreases in enthalpy for the stages ($\sum \Delta h_{ss}$) to the isentropic decrease in enthalpy for the turbine (Δh_{st}) is commonly called the *reheat factor*; thus

$$\mathcal{R} = \frac{\sum \Delta h_{ss}}{\Delta h_{st}}, \quad [78]$$

where \mathcal{R} denotes the reheat factor. It is a quantity greater than unity. It can be computed for any turbine with a known distribution of stage efficiencies and with known inlet state and exhaust pressure. Values of the reheat factor according to E. L. Robinson for steam turbines with uniform stage efficiency are shown in Fig. 90.

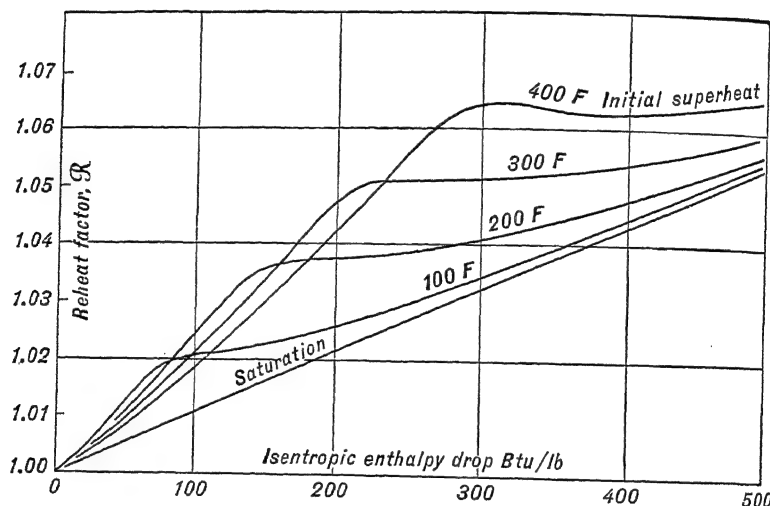


FIG. 90. Reheat Factors for an Infinite Number of Stages Each Having an Efficiency of 80 Per Cent

The reheat factor $\mathcal{R}_{N\eta}$ for N stages each having the efficiency η , is given by

$$(\mathcal{R}_{N\eta} - 1) = (\mathcal{R} - 1) \left(1 - \frac{1}{N}\right) (1 - \eta) / (1 - 0.8),$$

where \mathcal{R} denotes the ordinate in the figure. From E. L. Robinson, *Mech. Eng'g*, Vol. 50 (1928), p. 155.

The relation between the efficiency of a turbine of uniform stage efficiency and the efficiency of its stages is found by combining [75], [76], and [78] to be

$$\eta_t = \mathcal{R} \eta_s. \quad [79]$$

It is common practice in turbine design to calculate an approximate value of the required rate of fluid flow by means of the reheat factor.

First an estimated average value of η_s for the stages of the turbine is substituted into [79] along with an appropriate value of the reheat factor. The resulting turbine efficiency in combination with the desired power, the initial state, and the final pressure yields the rate of flow: thus, with the aid of [76] we get

$$w = \frac{P}{W_t} = \frac{P}{\eta_t \Delta h_{st}},$$

where P denotes the desired power. With the approximate flow known it is possible to select dimensions of nozzles and buckets upon which the efficiencies of the individual stages depend. The efficiencies corresponding to the selected dimensions may now be used to determine a condition curve and, through [74], the work per unit mass of fluid. This quantity with the desired capacity yields a second approximation to the rate of flow which is usually entirely adequate for determining, through stage dimensions, the stage efficiencies.

Wheel Speed

Let us define a quantity y as the ratio of the wheel speed of a stage to the characteristic velocity V_0 . Thus

$$y = \frac{W}{V_0}.$$

It follows from this and the definition of V_0 , [71], that for negligible V_a

$$W = y\sqrt{2g\Delta h_{ss}}.$$

For a turbine made up entirely of stages of one type, say, either the impulse type or the reaction type, y has approximately the same value for all stages. Therefore, we may write for such a turbine

$$\sum W^2 = 2gy^2 \sum \Delta h_{ss},$$

or, by [78],

$$\sum W^2 = 2gy^2 \mathcal{R} \Delta h_{st}, \quad [80]$$

where \sum denotes a summation of the quantities indicated by the symbol that follows it for all stages of the turbine.

The value of Δh_{st} depends upon the initial state and the final pressure of the fluid, and the value of \mathcal{R} on the same quantities and on the stage efficiencies and the number of stages. But with neither of the two latter does \mathcal{R} change rapidly (see Fig. 90); so that the value of $\sum W^2$ for maximum efficiency is virtually fixed by three things: the initial state, the final pressure, and the type of stage. It is essentially independent of the capacity of the turbine or the number of revolutions of the shaft per unit time.

The required magnitude of $\sum W^2$ may be provided either by a number of stages of small diameter at high angular velocity, or by the same number of stages of large diameter at low angular velocity. The weight of the turbine, and therefore its cost, will decrease with increase in angular velocity. However, for a given capacity the angular velocity cannot be increased indefinitely without encountering mechanical instability in the form of shaft vibration.

For any one angular velocity the value of $\sum W^2$ varies directly as nD^2 , where n denotes the number of stages and D a mean diameter. Since nD^2 is also an approximate measure of the volume of the turbine structure, it follows that for constant angular velocity $\sum W^2$ is an approximate measure of the weight and, therefore, of the cost of the turbine. For this reason, a manufacturer will never provide a larger value of $\sum W^2$ than is necessary to reach maximum efficiency; and he will in general provide less, for near the point of maximum efficiency the increment in efficiency corresponding to an increment in $\sum W^2$ is not great enough to justify the corresponding increase in cost. Moreover, the most economical value of $\sum W^2$ will be lower for turbines of low capacity than for turbines of high capacity; and it is largely because of this fact that the efficiency of turbines increases, as a rule, with capacity.

For the same inlet state and final pressure it is indicated by [80] that $\sum W^2$ for maximum efficiency varies directly as y^2 . Letting subscript i denote values for a pure impulse turbine and subscript r a pure reaction turbine, we get

$$\begin{aligned}\frac{\sum W_i^2}{\sum W_r^2} &= \frac{y_i^2}{y_r^2} \\ &= \frac{(\frac{1}{2})^2}{(1/\sqrt{2})^2} \\ &= \frac{1}{2}.\end{aligned}$$

It follows that an impulse turbine may have a considerably lower value of $\sum W^2$ (less wheel speed) than a corresponding turbine of the reaction type. It does not follow, however, that an impulse turbine costs half as much as a reaction turbine of the same efficiency, because the drum type of construction results in lower cost per stage.

An analysis similar to that just given shows how the two-row stage reduces the cost of a turbine. Comparing the value of $\sum W_2^2$ for a turbine made up of two-row stages with that of an impulse turbine, we get

$$\begin{aligned}\frac{\sum W_2^2}{\sum W_i^2} &= \frac{(1/4)^2}{(1/2)^2} \\ &= \frac{1}{4}.\end{aligned}$$

and comparing with the reaction turbine,

$$\begin{aligned}\frac{\sum W_2^2}{\sum W_r^2} &= \frac{(1/4)^2}{(1/\sqrt{2})^2} \\ &= \frac{1}{8}.\end{aligned}$$

Capacity of Multistage Turbines

However it may be distributed throughout the turbine, the amount of wheel speed, or $\sum W^2$, is virtually fixed by the initial state, final pressure, and type of stage, as indicated by [80], and is independent of the capacity of the turbine. The rotor of a turbine of high capacity will differ from that of a turbine of low capacity only in the radial heights of nozzles and buckets. In the high-pressure stages of the turbine these heights are small and a variation in their magnitude of two to one would make little difference in the appearance of the stages or in the dimensions of the casing which encloses them. Therefore, the patterns from which the high-pressure end of the casing is made may be used without alteration for turbines varying widely in capacity.

On the other hand, the nozzles and buckets of the low-pressure stages may be long relative to the stage diameters. To double their length might require major changes in the low-pressure end of the casing, and might at times be impracticable if bucket stresses become too large or if the buckets become so flexible as to be mechanically unstable.

Suppose, then, that a multistage steam turbine has been designed conservatively for a capacity of 10,000 kw. It is possible to make a second turbine with a capacity of 15,000 kw from these same designs and from the same patterns, provided that the radial heights of all nozzles and buckets are increased by half or as nearly by half as the design of the casing permits. The desired increase can be realized in full in the high-pressure stages, but in the stages of lowest pressure hardly at all. This second turbine will have a capacity of 15,000 kw, one-half larger than that of the first, though it will cost very little more than the first. But it will also have a high leaving loss — that is, the velocity of the steam will be high at the exit from the buckets of the last stage.

The capacity of turbines of a given design may be increased by this method up to the point where the magnitude of the leaving loss justifies the cost of a turbine with longer buckets on the last-stage wheel. However, the length of the buckets cannot be increased indefinitely without encountering mechanical limits which are set by the strength and stiffness of the bucket structure. When these limits are reached, then the limit of capacity for a single-casing turbine is also reached. Today that limit is about 150,000 kw. Further increase in capacity may be realized

by providing in the turbine two last-stage wheels instead of one, and leading one-half of the fluid stream to each. Such a turbine is called a *double-flow* turbine and it commonly has two casings: one for the high-pressure stages and one for the two sets of low-pressure stages, with steam admitted at the middle of the latter casing and discharging at both ends.

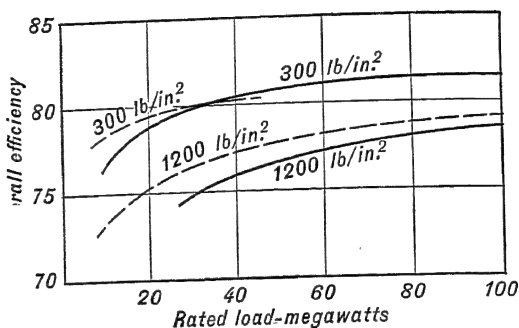


FIG. 91. Variation in Efficiency of Turbine-Generator Units of the General Electric Company

Condensing turbines, initial superheat 300 F. Full lines 1800 rpm. Dash lines 3600 rpm. Initial pressures given on curves. From Warren and Knowlton, *Trans. A.S.M.E.*, Vol. 63 (1941), p. 128.

The greater radial heights in the turbines of higher capacity result in an increase in the efficiency of the turbine, which can be accounted for by a reduction in the relative importance of frictional effects at the ends of the nozzle and bucket passages. Moreover, as was mentioned above, a turbine of higher capacity is generally provided with more wheel speed. For these reasons, principally, turbines of high capacity are more efficient than turbines of low capacity. The dependence of efficiency on capacity is shown in Fig. 91.

Comparison of the Reciprocating Engine and the Turbine

The capacity of a reciprocating engine of a given size increases with the number of working strokes that can be accomplished in unit time, that is, with the piston speed. In practice the piston speed is limited by the effects of throttling through ports, because these effects increase in importance with increase in speed.

When the maximum practicable speed is attained the capacity of the reciprocating engine can be increased only by increasing the dimensions of the engine. These become so large for a capacity of 10,000 kw that this figure has seldom been exceeded.

The steam turbine, on the other hand, is well adapted to capacities

more than ten times as great. In fact at 10,000 kw it is only beginning to realize the high efficiency of which it is capable, as is shown by Fig. 91.

A chart showing the efficiency of reciprocating engines as a function of capacity would differ little from Fig. 91, except that the range of values of the abscissa would be a small fraction of that of Fig. 91. If both were plotted to the same scale the result would be something like Fig. 92, which shows that the reciprocating engine is preferable at low capacity and that the turbine is without competition at high capacity.

The turbine is a device which must operate at high speeds of rotation, because by this means it is kept to reasonable dimensions at high capacity and to reasonable cost at low capacity. The reciprocating engine operates at relatively low speeds. Therefore, it is commonly employed to propel cargo ships, to drive locomotives, and to turn line shafting, all of which are tasks requiring no large amount of power and relatively low speed. The turbine, on the other hand, may be employed to drive an electrical generator which can operate at high speed and absorb a large amount of mechanical power. It is also used to drive centrifugal pumps and compressors, largely because they are high-speed devices. If it is to drive the propeller of a ship or the wheels of a locomotive it must be provided with reduction gearing.

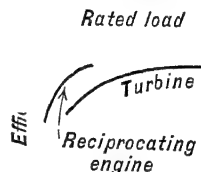


FIG. 92

PROBLEMS

1. Show that for reversible stages having zero angles the wheel speed for maximum work is given by the expression

$$\frac{W}{V_0} = \frac{1}{2\sqrt{1-x}},$$

where x denotes $\Delta h_{sb}/\Delta h_{ss}$.

2. (a) Show that the efficiency of a zero-angle stage of the pure reaction type which is reversible and adiabatic is given by the expression

$$\eta = 1 - (y - \sqrt{1 - \sqrt{2}y + y^2})^2,$$

where y denotes W/V_0 .

(b) Find a corresponding expression for a pure impulse stage.

(c) Find a corresponding expression for a stage for which

$$\frac{\Delta h_{sb}}{\Delta h_{ss}} = 1.$$

3. Show that in general the value of W/V_0 for maximum efficiency of a reversible, zero-angle, impulse turbine stage is $1/2n$, where n denotes the number of moving rows of buckets.

4. Show that a coefficient of velocity greater than unity would be impossible in view of the Second Law.

5. A turbine nozzle with well-rounded entrance has a minimum cross-sectional area (throat area) of 1 sq in. Calculate the discharge through this nozzle for pressure ratios of 0.9, 0.8, 0.7, 0.6, 0.58, 0.56, 0.54, 0.4, 0.3, 0.2, 0.1 for initially dry saturated steam at the following pressures: 50, 100, 200, 500, 1000, 1500, 2000, 2500, 3000 lb/sq in. abs. Calculate for the same pressures for steam initially at 700 F.

Assume the discharge coefficient to be unity and the approach velocity to be negligible.

6. Determine the exit area of a nozzle which will discharge 5000 lb of steam per hour. The initial steam pressure is 200 lb/sq in. abs, the initial steam temperature is 700 F. The pressure is 160 lb/sq in. abs in the exit plane of the nozzle. The steam approaches the nozzle with a velocity of 448 ft/sec. The discharge coefficient is unity.

7. If the pressure had been 80 lb/sq in. abs in the exit plane of the nozzle in the preceding problem how much exit area would be required? Would this area be the minimum cross-sectional area in the nozzle? If not, find the magnitude of the minimum area.

8. Design a nozzle passage of circular cross section to have equal pressure drops for equal increments of length. The initial pressure ahead of the nozzle is 300 lb/sq in. abs, the initial temperature 700 F, the final pressure is 1 in. Hg abs, and the flow is to be 1 lb./sec. Assume a constant-entropy expansion.

Plot against the distance through the nozzle:

(a) The static pressure in the stream.

(b) The velocity of the stream.

(c) The specific volume of the steam.

(d) The cross-sectional area of the stream.

(e) The diameter of the stream.

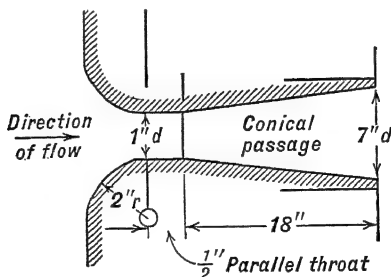
(f) The rate of flow per square inch of cross-sectional area.

(g) The temperature or quality of the steam.

(h) Ratio of cross-sectional area of the stream to the minimum cross-sectional area of the passage.

9. What are the critical pressure ratio and the critical velocity for the above conditions?

10. Plot the quantities (a) to (h) for initial conditions of problem 8 against distance along the nozzle for a nozzle with dimensions as shown in the sketch.



11. An impulse stage in a 10,000-kw turbine operates between 100 lb/sq in. abs 500 F and 80 lb/sq in. abs when the steam flow is 100,000 lb/hr. The velocity ap-

proaching the nozzle is 224 ft/sec; the pitch diameter is 4 ft. The nozzle angle is to be 12 degrees, and the edge factor 10 per cent. Calculate the nozzle radial height for the stage.

12. Steam enters a steam-turbine bucket at a relative velocity of 600 ft/sec and at a relative angle to the plane of the wheel of 27 degrees. The bucket velocity coefficient is 90 per cent; the bucket exit angle is 25 degrees. There is no drop in pressure across the bucket. What is the tangential force on the turbine bucket per pound of steam per second?

13. Steam leaves a turbine nozzle at an absolute velocity of 1070 ft/sec and at an absolute angle to the plane of the wheel of $14^{\circ} 45'$. The wheel velocity is 500 ft/sec. The absolute velocity of the steam leaving the wheel is 228.5 ft/sec and the absolute angle to the plane of the wheel is $87^{\circ} 22'$ forward running (tangential component in the direction of wheel rotation).

(a) What is the tangential force on the turbine bucket per pound of steam per second?

(b) How much power in kilowatts is being delivered to the turbine wheel by the steam if the steam flow is 100,000 lb/hr?

If the initial steam condition before the nozzles of this stage is 100 lb/sq in. abs and 500 F, the steam velocity there is 200 ft/sec, and the pressure before and after the buckets of the stage is 79 lb/sq in. abs.

(c) What is the nozzle velocity coefficient?

(d) What is the nozzle-bucket efficiency?

14. A single-stage impulse turbine is to be designed. The initial steam condition is 100 lb/sq in. abs 500 F, and the velocity approaching the nozzles is negligible. The exhaust pressure is 15 lb/sq in. abs. The nozzle angle is to be 15 degrees and the nozzle velocity coefficient is 95 per cent. The bucket exit angle is 30 degrees and the bucket velocity coefficient is 85 per cent.

(a) What is the value of W/V_0 when the wheel speed is 1100 ft/sec?

(b) How much power is delivered to the wheel by the active buckets at a wheel speed of 1100 ft/sec if the steam flow is 5000 lb/hr?

(c) At what wheel speed and what value of W/V_0 would the maximum power be delivered to the wheel?

(d) What would be the maximum power?

15. A pure impulse stage is to be designed with steam conditions, velocity before the nozzles, and nozzle angle as in problem 14. The bucket exit angle is to be 25 degrees, the nozzle velocity coefficient is 96 per cent, and the bucket velocity coefficient 90 per cent.

(a) Plot the nozzle-bucket efficiency against W/V_0 .

(b) At what W/V_0 is the efficiency a maximum?

(c) At what W/V_0 is the kinetic energy leaving the bucket a minimum?

(d) Plot relative entrance angles for the stream entering the bucket.

(e) Plot bucket exit height/nozzle exit height, assuming equal edge factors.

16. A reaction-turbine stage operates between 100 lb/sq in. abs 500 F and 80 lb/sq in. abs. The velocity approaching the nozzle is 250 ft/sec. The nozzle and bucket designs are identical with 90-degree entrance angles, 20-degree exit angles, 94 per cent velocity coefficients, and 100 per cent discharge coefficients.

(a) If the isentropic enthalpy drops across the nozzle and across the bucket are maintained equal, at what W/V_0 and what wheel speed will the bucket work be a maximum?

(b) At that wheel speed what is the ratio of bucket exit height to nozzle exit height? Assume equal gaging.

(c) An impulse stage reaches its maximum efficiency at a W/V_0 of approximately 0.49. What would be the ratio of the isentropic enthalpy drop in an impulse stage with wheel speed as in (a) to that of this reaction stage when both are working at maximum efficiency?

Find the axial thrust applied by steam to the buckets and their shrouding per unit rate of flow (per pound of steam per second) for the following two cases:

(d) The shroud and root of the bucket are parallel and form cylindrical boundary surfaces which are extended so as to run at close clearance from the nozzle face.

(e) The shroud is conical so that close clearance is maintained immediately around the nozzle annulus.

Neglect the effects of edge thickness.

17. A simple four-stage impulse turbine operates between 100 lb/sq in. abs 500 F and 15 lb/sq in. abs. The stage pressures are 65, 40, 25, and 15 lb/sq in. abs. The efficiency of each stage is 70 per cent, and practically no kinetic energy from the preceding stage is available to the nozzles.

(a) What is the reheat factor?

(b) What is the overall turbine efficiency?

(c) What is the temperature or quality at the entrance to each set of nozzles?

(d) Find the nozzle areas per pound of steam per hour, assuming nozzle flow coefficients of 100 per cent.

18. (a) If the wheel diameter of problem 15 is 36 in., the arc of admission 45 degrees, the bucket radial height 2 in., the steam flow 250,000 lb/hr, calculate the rotation loss per pound of steam at the W/V_0 of maximum efficiency. Use the Stodola formula.

(b) What is the corresponding stage efficiency?

SYMBOLS

a	cross-sectional area of a passage, acceleration
A	axial thrust
b	width of a nozzle passage
c	constant
c_v	coefficient of velocity
c_w	coefficient of discharge
D	pitch diameter
e	edge factor
f	coefficient of friction
F	force
g	acceleration given to unit mass by unit force
G	mass flow per unit area
h	enthalpy per unit mass

Δh_{ib}	isentropic drop in enthalpy across the buckets
Δh_{in}	isentropic drop in enthalpy across the nozzles
J	
l	radial height
L	rotation loss
m	mass
p	pressure
P	power
r	radius
R	frictional force per unit area
\mathcal{R}	reheat factor
S	shear stress
T	torque
u	tangential component of velocity
v	specific volume
v_s	specific volume at a state corresponding to the pressure after a nozzle or bucket and the entropy before it
V_0	characteristic velocity of a stage = $\sqrt{2g\Delta h_{ss} + V_a^2}$
$V_{1, 4, 5, 8}$	absolute velocities in velocity diagram
$V_{2, 3, 6, 7}$	relative velocities in velocity diagram
w	mass flow per unit time
W	speed of a bucket
W_s	work to shaft per unit mass of fluid
W_x	work to moving blades per unit mass of fluid
x	reaction ratio (= $\Delta h_{sb}/\Delta h_{ss}$)
y	W/V_0
z	axial component of velocity

GREEK LETTERS

α	nozzle angle
γ	pitch
η	efficiency
ρ	mass density (= $1/vg$)
ω	angular velocity

SUBSCRIPTS

a	approach to nozzle
b	bucket
c	critical pressure ratio
d	disk
n	nozzle
s	constant entropy, stage
t	tangential component, throat of nozzle, turbine as a whole

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CHAPTER XII

HEAT-ENGINE CYCLES

The Ideal Heat Engine

Corollary 1 of the Second Law was stated on page 73 as follows: *It is impossible to construct a heat engine to work between two reservoirs, each having a fixed and uniform temperature, which will exceed in efficiency a reversible engine working between the same reservoirs.* If we let T_1 denote the absolute temperature of the reservoir at higher temperature (the source) and T_2 that of the reservoir at lower temperature (the sink), then we may write for the efficiency, η , of a reversible engine

$$\eta = \frac{T_1 - T_2}{T_1}.$$

This was shown on page 79 to be a consequence of the definition of the absolute thermodynamic scale of temperature.

It follows, therefore, that the most efficient heat engine will be a reversible one that receives all its heat at the highest temperature at which heat is available and rejects heat only at the lowest temperature at which a sufficiently large reservoir can be found.

In the selection of a source and a sink the mean temperature of the atmosphere may be taken as a reference temperature. It is true that the atmosphere varies in temperature both with time and with position on the surface of the earth. But at any one place and at any one time the atmosphere may serve as a virtually infinite reservoir, the temperature of which will be unaffected (except locally) by heat transfers which are comparable in magnitude to those employed in the largest of modern heat engines. Temperatures higher than the temperature of the atmosphere are sometimes encountered in nature, such as the temperature of a surface exposed to sunlight or the temperatures of certain subterranean regions. Temperatures appreciably lower than that of the atmosphere are found less often, that of water at the bottom of deep tropical seas being one example.

Any of these natural temperature differences may be used to produce work, but they are commonly so small or so inaccessible that they cannot be exploited economically. Much greater temperature differences can be obtained in any desired location at moderate cost by means of a

chemical reaction. Commonly this takes the form of the oxidation of carbon or hydrocarbons such as coal, oil, or gas, and results in a marked rise in the temperature of the products of oxidation above that of the atmosphere. No chemical reaction is known which will produce a fall in temperature comparable in magnitude to the rise accompanying the oxidation of coal and for which the reactants are as abundant or as cheap as coal and oxygen.

Let us assume, now, that by means of a chemical reaction or otherwise a single reservoir may be devised which can be continuously maintained at a temperature different from that of the atmosphere regardless of the flow of heat from it (if it is at a higher temperature) or to it (if it is at a lower temperature).

Let us assume further that the atmosphere is the only available reservoir whose temperature remains unchanged when heat is rejected to it or withdrawn from it in large quantities over a long period of time.

Within any device which employs these two reservoirs, levels of temperature that are intermediate between the temperatures of the reservoirs may be maintained; and levels of temperature that are outside the range so established may also be maintained provided that some sort of heat pump or refrigeration machine is incorporated in the device. Nevertheless, *the efficiency of any reversible heat engine operating between the two reservoirs cannot be exceeded by the efficiency of any other device regardless of its complexity.* For, if a more efficient device were discovered, it would only be necessary to reverse the operation of the reversible engine in order to provide a heat pump which in combination with the device in question would constitute a perpetual-motion machine of the second kind. No advantage will be realized, therefore, in rejecting heat from an engine at a temperature below that of the atmosphere if the temperature of the source is above that of the atmosphere.

The most common source of heat employed in the production of power is a stream of products of the combustion of coal. Let us assume that a reasonable temperature for such products is about 3500 F, and that a reasonable temperature for the environment of a power plant (air or water) is about 50 F. Then the best efficiency, η_m , that could be realized by a heat engine is

$$\begin{aligned}\eta_m &= \frac{3500 - 50}{3500 + 460} \\ &= 87 \text{ per cent.}\end{aligned}$$

No existing heat engine has an efficiency that approximates this figure. In fact, the best modern heat engines attain efficiencies hardly in excess of 30 per cent.

A large part of the discrepancy between the possible efficiency of 87 per cent and the realized efficiency of 30 per cent can be accounted for in that no heat engine has yet been devised which can receive heat at a temperature as high as 3500 F. In fact, at this temperature most engineering materials are liquid and none are strong enough to constrain a fluid at relatively high pressure. Therefore, the state of the art and science of metallurgy determines an upper limit to the temperature at which a heat engine — that can be constructed at reasonable cost and operated with confidence — can receive heat. That limit today is slightly less than 1000 F. Thus, the most efficient heat engine would be limited to an efficiency of

$$\frac{1000 - 50}{1000 + 460} = 65 \text{ per cent,}$$

which still is more than twice the efficiency realized in practice.

To realize an efficiency of 65 per cent within the restrictions stated, the following conditions must be met: first, all heat that flows to the engine must be received by the working fluid at a temperature of 1000 F; second, all heat rejected by the engine must flow from the working fluid at a temperature of 50 F; and third, the operations of the engine must be completely reversible.

The first and second conditions might be met by an engine working, for example, on the Carnot cycle; but the third condition cannot be met by any real engine. The effects of departure from reversibility are, however, of more consequence in some types of engines than in others.

In Fig. 93 is plotted on a p - v diagram a Carnot cycle for air. The work delivered by the gas to the piston in the course of its outward stroke

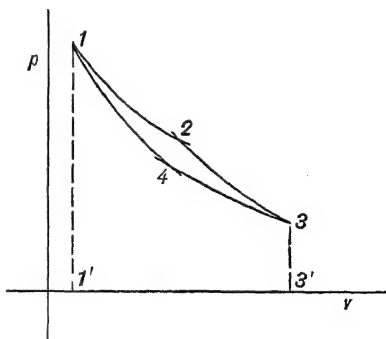


FIG. 93. The Carnot Cycle

is the area 1233'1'1; and the work done by the piston on the gas in the return stroke is the slightly smaller area 1433'1'1. The net work — that is, the useful work — of the cycle is the relatively small area 12341. Now the work that is expended in friction between piston and cylinder wall, and between journals and bearings in the external parts of the engine, will be some determinable fraction of the work delivered to the piston in the course of its outward stroke. Because of that friction the work which reaches the flywheel shaft (or whatever member it must ultimately reach in order to be useful) will be less than 1233'1'1 during

the outward stroke; and the work which must be received from the flywheel shaft for the return stroke will be greater than the area 1433'1'1. It is easy to see that the net work delivered to the flywheel shaft will vanish and even become negative for a friction effect which is only a small fraction of the work quantities employed in the cycle. For this reason, principally, the Carnot cycle has never been used in the commercial production of work.

The Stirling Air Engine

In the middle of the nineteenth century Stirling devised an air engine in which the effects of irreversibility were less than in the Carnot cycle. His cycle, which is shown in idealized form on the p - v diagram of Fig. 94, has a larger ratio of the net work to the work of each stroke than the Carnot cycle. It consists of two isometrics joined by two isotherms. Heat is taken from the source during the isothermal expansion at the higher temperature and is rejected to the sink during the isothermal compression at the lower temperature. In order to avoid heat exchange between the working fluid and the source or sink while the fluid is at intermediate temperatures the two isometric processes, 23 and 41, are executed with the aid of a *regenerator*, which is a series of heat reservoirs that are not supplied with energy from any outside source. The gas

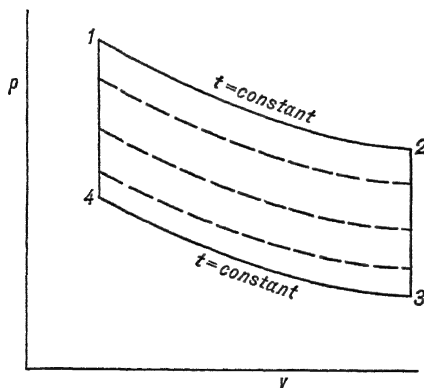


FIG. 94. The Stirling Cycle

is cooled in the process 23 by successive contact with parts of the regenerator which are at temperatures ranging from that of the source to that of the sink; it is heated in the process 41 by contact with the same parts in reverse order. Now, if there are an infinite number of such parts each with infinite heat capacity and each completely insulated from the others, and if the specific heat of the gas at constant volume is the same at each temperature for both isometrics, then the processes 23 and 41 may be entirely re-

versible and completely independent of the source and sink. The cycle is then a reversible cycle working between the temperatures of source and sink, and its efficiency is, therefore, identical with that of a Carnot cycle.

Despite its high efficiency the Stirling engine has failed to come into

general use. In order to get rapid transfer of heat from the source to the working fluid it was necessary to heat the chamber walls to a temperature which no available materials could long withstand. Creditable performance of the engine was obtained only at extremely low speeds for which the rate of heat transfer was small — and for which the power produced was extremely small in view of the cost of the engine.

The Rankine Cycle

The large negative work of the Carnot cycle, and the correspondingly small net work, can be avoided if a condensable vapor is employed as the working fluid. In Fig. 95 is shown, for example, a cycle 12341 for water confined by a piston in a cylinder. Saturated liquid, 1, at the temperature of the sink is compressed reversibly and adiabatically to a state 2 at higher pressure. Then heat is added from the source while the fluid expands at constant pressure until it is completely transformed to the vapor phase in the saturated state 3. Next, the cylinder is isolated from source and sink and the fluid expands reversibly and adiabatically to the sink temperature at state 4. Finally, the piston returns to its original position and the fluid returns at constant pressure to its initial state while heat flows to the sink. If the temperature of vaporization is 400 F and the temperature of condensation 50 F the net work of this cycle is more than 90 per cent of the work done in the outward stroke, and the cycle is not, therefore, sensitive to small degrees of irreversibility. For this reason, principally, a condensable vapor is the working fluid in virtually all practicable heat-engine cycles. Commonly, the changes of state indicated in Fig. 95 are accomplished wholly or in part in steady-flow processes.

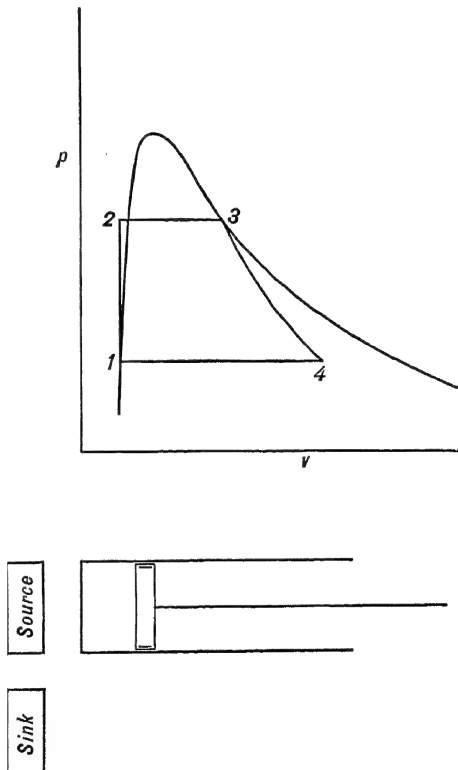


FIG. 95. The Rankine Cycle

If water is the working fluid the cycle just described, which is illustrated in Fig. 95, is called a Rankine cycle. When it is plotted on a temperature-entropy diagram, Fig. 96, some of its defects become evident: First, that part, $22'$, of the heating process which precedes vaporization is carried out at temperatures less than the maximum temperature of the cycle. The efficiency of the cycle must, therefore, be less than the efficiency of the Carnot cycle corresponding to its extreme temperatures. Second, vaporization cannot be carried out at the highest temperature that modern metallurgy permits (the *metallurgical limit*, Fig. 96), which is approximately 1000 F. For the critical temperature of water is far below 1000 F — namely, 705 F — and therefore no process at constant pressure can coincide with a process at the maximum temperature.

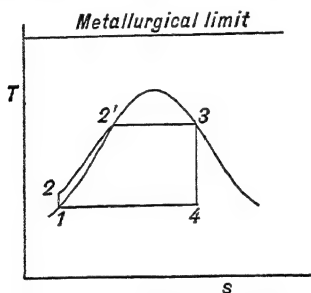


Fig. 96. The Rankine Cycle

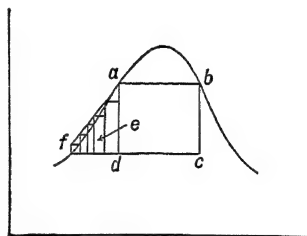


Fig. 97

These defects are made more evident by considering the Rankine cycle to be made up of a large number of Carnot cycles as illustrated in Fig. 97. In that figure the large Carnot cycle $abcd$ taken together with an infinite number of small ones such as e extending along the line of constant pressure in the liquid region from f to a makes a combination which is identical with the Rankine cycle in heat received and rejected and in work delivered. The efficiency of this combination — and, therefore, of the Rankine cycle — is determined by the efficiencies of the elementary Carnot cycles which are comprised within it. Improvement in the efficiency of the combination may be achieved by (a) adding Carnot cycles which are more efficient than the combination, (b) improving the efficiency of the constituent Carnot cycles, or (c) eliminating Carnot cycles which are less efficient than the combination. If we assume that the temperature of heat rejection is the temperature of the atmosphere, or as near that as economy permits, then items (a), (b), and (c) may be summed up by the statement that improvement in the efficiency may be achieved by *increasing the average temperature at which heat is received*.

Superheat

The average temperature at which heat is received may be increased appreciably by heating the vapor above the temperature of vaporization to as high as the metallurgical limit before delivering it to the engine.

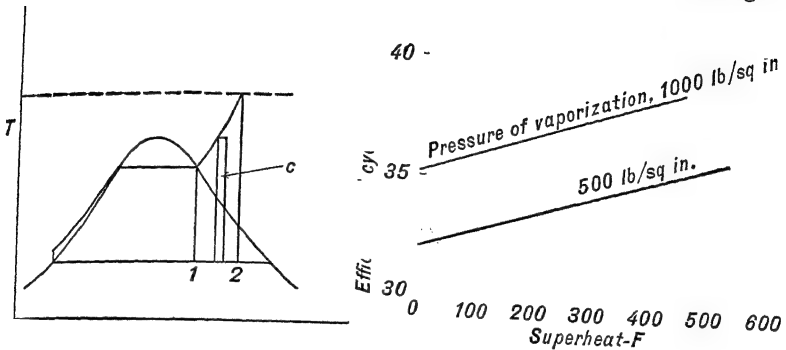


FIG. 98. The Effect of Superheat

In effect, this device adds to the Rankine cycle an infinite number of small Carnot cycles (c , Fig. 98), each of which is more efficient than the Rankine cycle, in accordance with item (a) of the preceding paragraph. The effect of superheat on the efficiency of the Rankine cycle is shown by the curves of Fig. 98.

With the consequent improvement in efficiency there goes a reduction in the amount of moisture contained in the vapor at the exhaust of the engine from that of state 1 of Fig. 98 to that of state 2. This effect is sometimes more important than the immediate gain in efficiency of the cycle, for in large central-station power plants the erosive effect of moisture on the blades of the turbine is so great that economic considerations set a definite limit to the ratio of liquid to vapor that can be tolerated. Today that limit lies at a proportion of liquid somewhat in excess of 10 per cent.

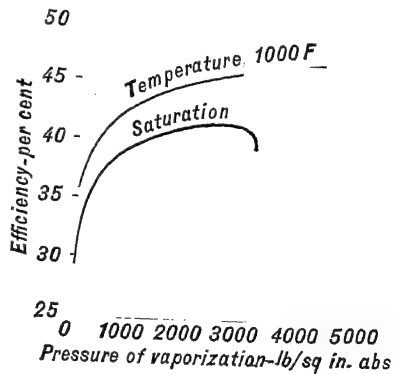


FIG. 99. Efficiency of the Rankine Cycle

The label on the curve indicates the condition before expansion.

High Pressure

The average temperature at which heat is received may be most readily increased by increasing the temperature of vaporization, because

the Carnot cycle *abcd* under the vaporization line of Fig. 97 is a major part of the Rankine cycle. The relation between the efficiency of a Rankine cycle without superheat and the pressure of vaporization is shown by the curve marked "Saturation" in Fig. 99, while that for a Rankine cycle with steam superheated to the metallurgical limit is shown by the curve marked "1000 F."

Since the latter curve continues upward to the highest pressure for which we have precise knowledge of the properties of steam — that is, well in excess of the critical pressure — the pressure at which steam is generated may be profitably raised until the increase in efficiency caused by further increase in pressure is offset by some accompanying disadvantage.

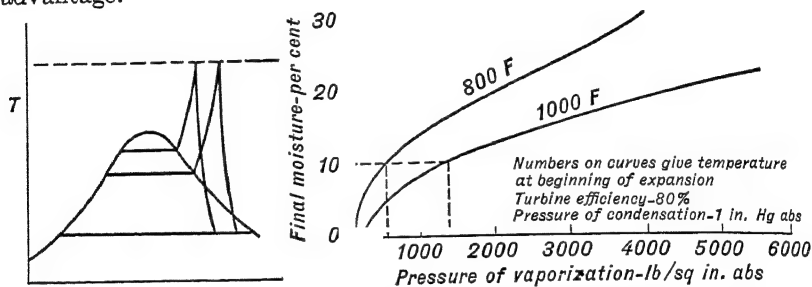


FIG. 100. The Effect of Pressure of Vaporization on Final Moisture

It was pointed out in the preceding section that the erosive effect of moisture on the blades of a turbine sets a limit to the ratio of liquid to vapor that can be tolerated in the final stages of the turbine. The temperature-entropy diagram of Fig. 100 shows graphically how an increase in the pressure of vaporization results in a marked increase in the moisture in the steam at the end of the expansion, provided that the temperature of the steam at the inlet to the turbine is not altered. In the same figure are shown curves which give moisture in the last stage of a turbine as a function of pressure of vaporization, for cycles working to metallurgical limits of 1000 F and 800 F having turbines of 80 per cent efficiency exhausting at a pressure of 1 in. of mercury absolute. They show that if 10 per cent moisture is the maximum that can be tolerated, then the highest pressure of vaporization is 550 lb/sq in. if the metallurgical limit is 800 F and 1400 lb/sq in. if the limit is 1000 F.

Now if the temperature of the steam supplied to the turbine is raised from 800 F to 1000 F at a pressure of 550 lb/sq in. the efficiency of the cycle, with a turbine of 80 per cent efficiency exhausting at 1 in. of mercury, increases from 30.8 per cent to 32 per cent, an improvement of 4 per cent. But if the increase in temperature is accompanied by the

maximum permissible increase in pressure, namely, to 1400 lb/sq in., the efficiency of the cycle increases from 30.8 per cent to 34.6 per cent, an improvement of $12\frac{1}{2}$ per cent. These figures demonstrate the effect of an increase in the temperature of vaporization.

Reheat

An upper limit to the moisture content of the steam leaving the turbine seems to imply an upper limit to the pressure of vaporization, which for a metallurgical limit of 1000 F is about 1400 lb/sq in. The efficiency would be limited in turn to the best that could be attained with steam conditions so restricted.

There is, however, a means of raising still further the pressure of vaporization (and, consequently, the efficiency) without exceeding the limiting value of moisture content. It is illustrated in Fig. 101. Steam is generated at a high pressure and superheated until the metallurgical limit is reached as shown by point *a* in Fig. 101. It is then expanded through the turbine to some pressure intermediate between the pressures of vaporization and condensation, whereupon it is returned to the source of heat and reheated, virtually at constant pressure, until its temperature is once more at the metallurgical limit. It is returned again to the turbine in state *b* of Fig. 101 and expanded to condenser pressure.

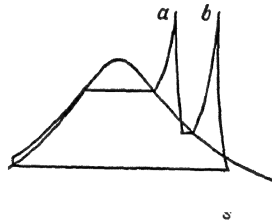


FIG. 101. The Reheat Cycle

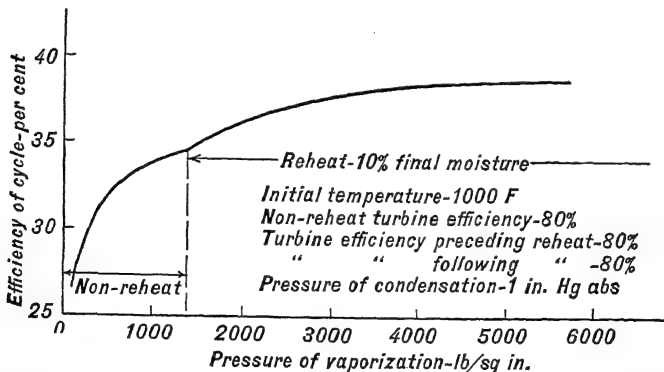


FIG. 102. Variation in Efficiency with Pressure of Vaporization

In Fig. 102 is shown the thermal efficiency of steam cycles as a function of the pressure of vaporization. For pressures below 1400 lb/sq in.

the final moisture content in the expansion is less than 10 per cent. Above 1400 lb/sq in. reheat is employed so as to keep the final moisture content at 10 per cent.

Since reheat involves a considerable increase in the cost of a power plant, it could be justified only by a marked increase in efficiency. It is probable, therefore, that in the example corresponding to Fig. 102 the pressure of a reheat station would be considerably in excess of 1400 lb/sq in. However, it probably would not exceed 3000 lb/sq in. because according to Fig. 102 the efficiency increases very slowly with increase in pressure beyond that magnitude.

Regenerative Feed-Water Heating

The devices so far discussed for increasing the efficiency of the Rankine cycle have consisted principally of means of increasing the temperature

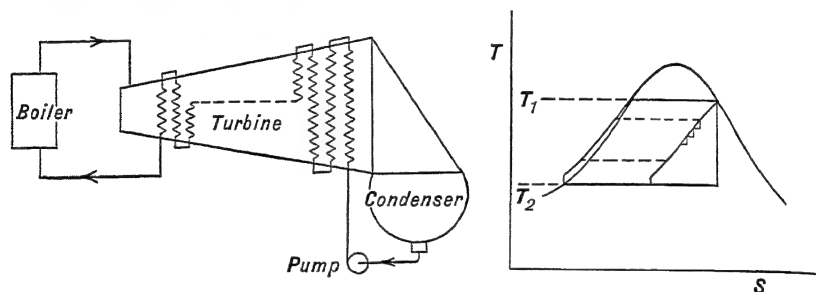


FIG. 103. A Reversible Regenerative Cycle in Which Heat Is Received at One Temperature Only and Heat Is Rejected at One Temperature Only

at which heat is added to the working fluid. An alternative means consists of decreasing the flow of heat which the working fluid receives at the lowest temperatures.

In order to simplify the discussion of this alternative, we shall consider a Rankine cycle without superheat, as shown in Fig. 103. Let us assume that the turbine through which the steam expands has an infinite number of reversible stages, and that the condensate coming from the condenser is pumped immediately to boiler pressure in a reversible adiabatic feed pump. Now, if the feed water leaving the pump is led to a heating coil installed in that turbine stage in which the steam is at an infinitesimally higher temperature than the temperature of the feed water, the liquid will leave the coil at this higher temperature if sufficient heating surface is provided. Next, the liquid is passed through a similar heater in the next higher stage where its temperature increases again by an infinitesimal amount, and so on until it leaves the last heater in the turbine at the temperature of the incoming steam.

Finally, it is led to the boiler where it is immediately vaporized without change in temperature.

Since the steam passing through the turbine is employed to heat the liquid between stages, the series of states it assumes may be represented by an infinite number of small steps, each of which consists of an isentropic and a constant-pressure process as illustrated in Fig. 103.

The entire cycle is reversible, because the direction of flow of the working fluid could be reversed, and with it the heat and work effects, with only infinitesimal changes in temperature levels. Thus the effects produced could be completely undone by reversing the direction of flow.* The efficiency of the cycle is, therefore, given by

$$\eta = \frac{T_1 - T_2}{T_1}$$

(where T_1 and T_2 are respectively the absolute temperatures of vaporization and condensation), as is required for any reversible engine working between two temperature levels by the definition of the absolute temperature scale.

The same conclusion may be arrived at from a different point of view. As the liquid is heated in a stage of the turbine the increase of entropy of unit mass of the liquid, ds_l , for each increment of temperature, is given to small quantities of the first order by

$$ds_l = \frac{dq}{T},$$

where dq denotes a positive number which is the amount of heat flowing from steam to liquid per unit mass of fluid passing any section and T is the temperature of the liquid leaving the heater (which is also the temperature of the steam in the stage). Since the liquid is heated in steady flow at constant pressure, $c_p dT_l$ may be substituted for dq , giving

$$ds_l = c_p \frac{dT_l}{T},$$

or

$$\frac{ds_l}{dT_l} = \frac{c_p}{T}, \quad [81]$$

where c_p denotes the specific heat of the liquid at constant pressure and dT_l the increase in temperature of the liquid in the heater. The change

* This statement implies that the temperatures of source and sink are respectively the temperatures of vaporization and condensation. Since this condition could be met without altering the cycle, the conclusions reached concerning the cycle are valid.

in entropy of unit mass of steam in the stage, ds_s , is given to small quantities of the first order by

$$ds_s = -\frac{dq}{T},$$

because the heat transferred from each unit mass of steam is identical with that transferred to each unit mass of liquid. The change in the temperature of the steam between two successive stages is numerically the same as the corresponding increase in temperature of the liquid, but it is opposite in sign. Denoting it by dT_s , we have

$$dT_l = -dT_s$$

and

$$dq = -c_p dT_s.$$

Making this substitution in the expression for ds_s and rearranging, we get

$$\frac{ds_s}{dT_s} = \frac{c_p}{T},$$

which in combination with [81] gives

$$dT_s \frac{ds_l}{dT_l}.$$

Thus, the slope of the expansion line on the temperature-entropy diagram is at each level of temperature identical with the slope of the line representing the heating of the liquid. It follows that the difference in entropy between the expansion line and the liquid line is the same at all temperatures and, in particular, at the temperatures corresponding to vaporization and condensation. Therefore, we may derive an expression for the efficiency of the cycle as follows:

$$\eta = \frac{q_1 - q_2}{q_1}$$

where q_1 denotes heat received in vaporization and q_2 heat rejected in condensation; but since,

$$q_1 = T_1 \Delta s$$

and

$$q_2 = T_2 \Delta s,$$

where T_1 and T_2 denote respectively the temperatures of vaporization and condensation and Δs denotes the entropy change at either

temperature, it follows that

$$\eta = \frac{T_1}{T_1}$$

This regenerative cycle is equal to the Carnot cycle in efficiency, but it is superior to the Carnot cycle in one respect: the ratio of net work to gross work (work of expansion) is much greater, and irreversibility arising from friction is therefore of less consequence.

When superheat is introduced the regenerative cycle cannot so readily be made reversible. A heat transfer from the superheated vapor will cause a decrease in the temperature of the vapor that is greater in magnitude than the corresponding increase in the temperature of the liquid, because the specific heat of the vapor is less than that of the liquid. Therefore, the liquid cannot be continuously heated reversibly by the vapor.* However, the departure from reversibility may not be so great as to discourage the use of heat exchange between superheated vapor and liquid.

Of course, the turbine postulated in the previous discussion is utterly unreal because it is reversible and because it has an infinite number of stages with infinite heat-transfer surface in each stage. The cycle which this turbine makes possible can be approximated in practice, however, by the relatively crude system of Fig. 104.

Here a single heater is employed instead of an infinite number of heaters. Steam from an intermediate stage is supplied to an external chamber through which the feed water passes on its way to the boiler. The temperature of the liquid may be raised in the heater almost to the tem-

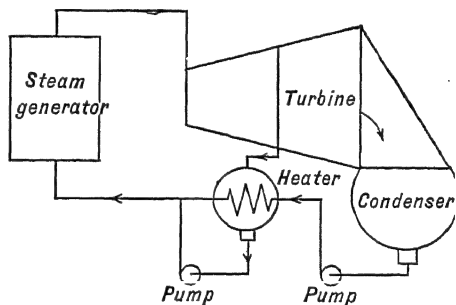


FIG. 104. Single-Heater Regenerative Cycle

perature of condensation of the vapor that heats it. The condensate formed in the heater is called the *drip*. It may be disposed of in various ways. In Fig. 104 it is pumped into the feed line after the heater.

The steam that is used to heat the feed water may be withdrawn from the turbine at any point between the turbine inlet and the turbine

*A completely reversible heat exchange can be accomplished in this case by substituting isentropic steps of compression for the isentropic steps of expansion of the usual regenerative cycle. When, in practice, the steps become finite no advantage can be realized from steps of compression. See Field, *Jl. Inst. Civil Eng'rs*, Vol. 10 (1938-39), p. 241.

exhaust passage. If we assume that the steam entering the turbine is saturated steam at boiler pressure and that the steam leaving it is a two-phase mixture at condenser pressure, then the liquid may be heated to any temperature up to the boiling point corresponding to boiler pressure. The condensate leaving a perfect condenser will be at the same temperature as the exhaust steam, so that if the heater is connected to the exhaust passage no heating of the feed water will occur and no gain in efficiency will result. At the other extreme, when the heater is con-

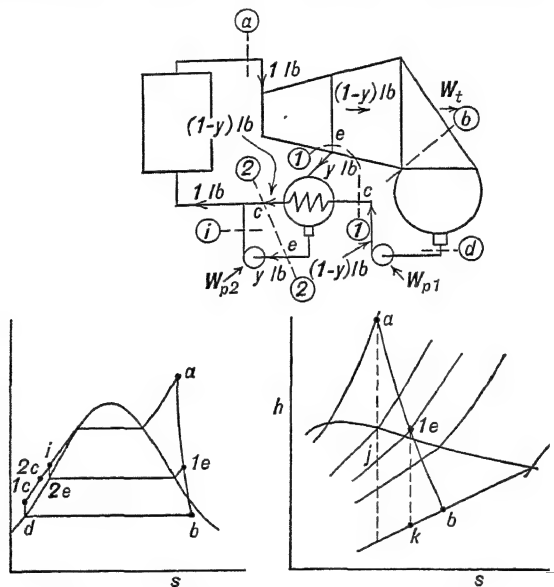


FIG. 105. Analysis of Regenerative Cycle

nected with the steam inlet the heat transfer to the feed water will be at a maximum; but no gain in efficiency will result because the steam that heats the feed water serves merely as a heat-transfer medium between the heat source (the products of combustion) and the feed water. Therefore, for these two extreme positions of the heater the gain in efficiency will be zero, while for some intermediate position it will reach a maximum. The position corresponding to maximum gain in efficiency may be found by computing the gain for various positions and plotting the gain against the position of the heater, or against the temperature to which the liquid is heated.

Analysis of the Single-Heater Regenerative Cycle

Consider the complete steady-flow heat engine shown in Fig. 105 in which a steam generator delivers superheated steam to a turbine which

exhausts it as a mixture of liquid and vapor to a condenser. The condensate leaves the condenser as a saturated liquid at condenser pressure and is pumped reversibly and adiabatically to boiler pressure in a feed pump which delivers the liquid to coils passing through a heater. The heater is supplied from an intermediate stage of the turbine with steam which condenses on the coils and leaves the heater as a saturated liquid at the pressure of the steam space in the heater. It is then pumped into the feed-water line which carries the liquid leaving the coils of the heater. The combined streams of liquid then pass to the boiler, which is part of the steam generator.

The processes experienced by the fluid in this heat engine are shown on the temperature-entropy diagram of Fig. 105. Steam enters the turbine in state a and flows to the stage from which steam is to be extracted, where its state is $1e$. At this point the stream is split into two parts. One part expands in the turbine to lower pressures, enters the condenser in state b , the feed pump in state d , and the heater in state $1c$. The other part enters the heater in state $1e$ and leaves it in the saturated liquid state $2e$, after which it is pumped to state i and mixed with the other stream before both are returned to the boiler.

Let us analyze by means of the energy equation of steady flow [5a] the processes which occur over the period of time required for unit mass of fluid to enter the turbine. We shall consider the heater as a whole to be the apparatus into and out of which fluid is flowing in two streams, that of the steam from the extraction stage and that of the feed water. For this apparatus $\sum \delta Q$, the heat transferred into the apparatus from its environment, may be approximately zero; and $\sum \delta W_x$, the work passing out of the apparatus to the environment, is likewise zero. If velocities and changes in height are negligible, we find from [5a] that the net flow of enthalpy into the apparatus is zero; that is, the enthalpy of the fluid entering the heater is equal to that of the fluid leaving it. If we let y denote the mass of fluid that passes out of the extraction stage while a unit mass of fluid enters the turbine, then [5a] becomes

$$yh_{1e} + (1 - y)h_{1c} = yh_{2e} + (1 - y)h_{2c},$$

where subscripts 1 and 2 denote respectively sections through entering and leaving streams, subscript e denotes the fluid extracted from the stage, and subscript c the liquid stream passing through the heater. It follows that

$$y = \frac{h_{2c} - h_{1c}}{h_{1e} - h_{2e} + h_{2c} - h_{1c}}. \quad [82]$$

In order to compute the value of y from [82] for various values of the pressure in the extraction stage, it is necessary to know in addition to the properties of the steam leaving the generator and the pressure in the condenser the entire condition curve of the turbine, as shown by ab in the Mollier diagram of Fig. 105. But once the value of y is known the efficiency of the cycle can readily be found.

EXAMPLE. Let us find the saving resulting from a single heater in a cycle like that of Fig. 105 to which the following data apply.

Steam generated at 300 lb/sq in. abs and 700 F	
Condenser pressure	= 1 in. Hg abs
Extraction stage pressure	= 30 lb/sq in. abs
Efficiency of that part of the turbine between inlet and extraction stage	= 80 per cent
Efficiency of that part of the turbine between extraction stage and condenser	= 75 per cent

Assume that the condensate leaving the condenser is in the saturated state corresponding to the pressure in the condenser, that the liquid leaving the coil of the heater and the drip leaving the heater are both at the temperature corresponding to the saturated state at the pressure of the extraction stage, and that compression in the two pumps is isentropic. For values taken from the steam tables in subsequent calculations the appropriate table in Keenan and Keyes is given in parenthesis.

Saturation temperature at 30 lb/sq in.	250.3 F (Table 1)
Enthalpy of condensate leaving condenser, h_d ,	47.05 Btu/lb (Table 1)
Entropy of condensate leaving condenser, s_d ,	0.0914 Btu/lb degree F (Table 1)
Entropy of liquid entering heater, s_{1e} ,	0.0914 Btu/lb degree F
Pressure of liquid entering heater	300 lb/sq in.
Enthalpy of liquid entering heater, h_{1e} ,	47.95 Btu/lb (Table 4)
The liquid leaves the heater coils at 300 lb/sq in. and 250.3 F	
Enthalpy of liquid leaving coils, h_{2c} ,	219.4 Btu/lb (Table 4)
Enthalpy of drip from heater, h_{2e} ,	218.8 Btu/lb (Table 2)

Using the symbols of Fig. 105 as subscripts to denote the corresponding states we have:

$p_a = 300$ lb/sq in.	$t_a = 700$ F	$h_a = 1368.3$	$s_a = 1.6751$ (Table 3)
$p_j = 30$ lb/sq in.		$h_j = 1146.9$	$s_j = 1.6751$ (Table 2)

Neglecting velocities, we get from the definition of the efficiency of the high-pressure end of the turbine

$$h_{1e} = h_a - 0.80 (h_a - h_j) = 1191.2 \text{ Btu/lb.}$$

Then, by [82],

$$y = 0.15.$$

Using subscripts in accordance with the notation of Fig. 105, we may write

for the work delivered by the turbine

$$W_t = h_a - h_{1e} + (1 - y) 0.75 (h_{1e} - h_k),$$

provided that velocities at *a* and *1e* are negligible. The state *k* is identified by the pressure; namely, 1 in. Hg, and by the entropy which is that of state *1e*; namely, 1.7361. The value of *h_k* is found from Table 2 to be 933.4. Substitution yields

$$W_t = 341.3 \text{ Btu/lb.}$$

The negative work of the cycle is given by

$$W_{p1} + W_{p2} = (1 - y)(h_{1c} - h_d) + y(h_i - h_{2e}),$$

where subscripts are used in accord with the notation of Fig. 105. Table 4 provides the necessary values, from which we get

$$W_{p1} + W_{p2} = 0.9 \text{ Btu/lb.}$$

Then the net work of the cycle is

$$W_t - (W_{p1} + W_{p2}) = 340.4 \text{ Btu/lb.}$$

The heat added to the fluid in the steam generator per pound of steam generated, *Q_g*, is

$$\begin{aligned} Q_g &= h_a - (1 - y)h_{2c} - yh_i \\ &= 1368.3 - 0.85 \times 219.4 - 0.15 \times 219.6 \\ &= 1148.9 \text{ Btu/lb.} \end{aligned}$$

The heat supplied per kilowatt-hour of work delivered is

$$1148.9 \times 3412.8 / 340.4 = 11,520 \text{ Btu/kw-hr,}$$

and the efficiency of the cycle is

$$340.4 / 1148.9 = 29.6 \text{ per cent.}$$

Now, if there had been no extraction of steam for feed-water heating all the liquid fed to the steam generator would be in a state corresponding to section *1c*. The heat added to the fluid in the steam generator per pound of steam generated would then be

$$h_a - h_{1c} = 1368.3 - 47.95 = 1320.3 \text{ Btu/lb,}$$

and the work done by each pound of fluid passing through the turbine would be

$$\begin{aligned} h_a - h_b &= h_a - h_{1e} + 0.75 (h_{1e} - h_k) \\ &= 177.1 + 193.3 \\ &= 370.4 \text{ Btu/lb.} \end{aligned}$$

Then the net work of the cycle is the work delivered by the turbine less the feed-pump work. Using subscripts in accord with the notation of Fig. 105,

we have

$$\begin{aligned}\text{Net work} &= 370.4 - (h_{1c} - h_d) \\ &= 370.4 - 0.9 \\ &= 369.5 \text{ Btu/lb,}\end{aligned}$$

which is appreciably larger than the net work of the extraction cycle per pound of steam generated. The heat supplied per kilowatt-hour of work delivered is

$$1320.3 \times 3412.8 / 369.5 = 12,195 \text{ Btu/kw-hr.}$$

With extraction of steam for heating the feed water the heat supplied was 11,520 Btu/kw-hr, and the saving resulting from regenerative heating is, therefore,

$$\frac{12,195 - 11,520}{12,195} = 5.5 \text{ per cent.}$$

If similar calculations are made for various pressures in the extraction stage the saving will be found to be related to the temperature of the feed water after the heater in the manner indicated by the lowest curve of Fig. 106. For a single heater it reaches a maximum when the feed water is heated to a temperature about half way between that of the condenser and that of the boiler.

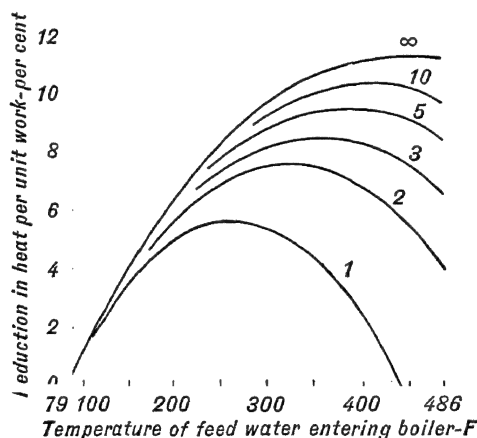


Fig. 106. Saving Resulting from Regenerative Feed-Water Heating

Pressure of vaporization, 600 lb/sq in. abs; temperature of steam leaving steam generator, 800 F; pressure of condensation, 1 in. Hg abs. Figures on curves indicate the number of heaters and extraction points. From Keller, *Power Plant Eng'g*, Vol. 43 (1939), p. 122, by permission of the General Electric Company.

Multiple-Heater Regenerative Cycle

The regenerative cycle with a single heater is merely a crude approximation to that with an infinite number of heaters. The approximation may be refined by adding one or more heaters spaced along the length

of the turbine. Following the principles laid down for the cycle with a single heater, one can readily calculate the efficiency of a cycle with any prescribed number of heaters.

The curves of Fig. 106 were so calculated. They show the relation between the gain in efficiency resulting from regenerative heating and the temperature of the feed water leaving the heater of highest temperature. They also show how the temperature to which the feed water is heated may be increased to advantage when the number of heaters is increased.

In central power stations the number of regenerative heaters may range from one to five or six. In the smaller power plants employed on locomotives or in ships the number seldom exceeds two.

The Ideal Fluid for Heat Engines

The various devices discussed in the preceding paragraphs are effective only to a limited degree. Imagine a heat engine in which liquid water is heated regeneratively to the temperature of vaporization in the boiler, so that heat is added only to vaporize the water and to superheat it. If the vapor is generated and superheated at 1300 lb/sq in. and the metallurgical limit is 1000 F, the maximum value for the average temperature at which heat is received is only 606 F. Alternatively, if the vapor is generated and superheated at 2300 lb/sq in. and reheated to the metallurgical limit at 200 lb/sq in., the average temperature at which heat is received is about 710 F. Both these values of the average temperature are far less than the temperature at the metallurgical limit because most of the heat is received by the fluid at the temperature of vaporization.

At 2300 lb/sq in. the temperature of vaporization is 656 F, which is within 50 degrees of the critical temperature beyond which heat cannot be added at constant temperature and at constant pressure as well. Therefore, a further rise in the pressure of vaporization will cause little increase in the average temperature of heating. It appears, then, that the characteristics of the working fluid set an upper limit which the average temperature of heating cannot readily be made to exceed. Higher average temperatures, and correspondingly higher efficiencies, can be realized with the usual devices only if a fluid with different characteristics is employed. The particular characteristic desired is a *critical temperature well in excess of the metallurgical limit.*

Of course, other requirements must be fulfilled, and the specifications for an ideal fluid for heat engines would include the following items:

- (a) The critical temperature should be well in excess of the metallurgical limit, for reasons given above.

(b) The triple-point temperature should be less than the lowest temperature attained by the available heat sink, because a solid is difficult to convey between regions of different pressure.

(c) The vapor pressure should be moderate at the metallurgical limit, in order to avoid extreme stresses in the container walls at the high temperatures.

(d) The vapor pressure should not be too low at the temperature of the sink, else non-condensable gases that leak into the system or that enter as solutes in the fluid must be pumped out from a region of very low pressure at great cost; moreover, very low pressures are accompanied by high specific volumes of the working fluid, and these require large and expensive equipment.

(e) The latent heat, or change in enthalpy during vaporization, should be large in comparison with the heat supplied to the liquid, so that regenerative devices will not greatly increase the cost of the engine.

(f) The entropy of the saturated vapor should be nearly the same at the temperature of the sink and at the metallurgical limit, for a great difference in one direction would require that some heat be rejected above the temperature of condensation, while a great difference in the other direction would require excessive moisture at the end of the expansion.

These are the thermodynamic specifications. In addition to these there are two indispensable requirements: first, that the fluid must be completely stable under all conditions likely to be encountered — that is, it must not dissociate or crack in distillation; second, it must not dissolve or react chemically with the materials available for retaining it. Furthermore, it should be cheap, abundant, and non-poisonous.

No single fluid has yet been discovered that fulfills all these specifications. It will be noted that water satisfies, or nearly satisfies, specifications (b), (d), (e), and (f), but it utterly fails to satisfy (a) and (c). Mercury, on the other hand, satisfies (a), (b), and (c) entirely (critical temperature > 2800 F, triple-point temperature -38 F, vapor pressure at 1000 F 180.4 lb/sq in.). It satisfies (e) and (f) very nearly; but it fails to satisfy (d), it is neither cheap nor abundant, and its vapor is highly poisonous in any appreciable concentrations. In the absence of a fluid which combines the merits of both,* water and mercury may be used to supplement each other so that in combination they satisfy all the thermodynamic specifications.

* See Table VIII, page 355, for critical data on numerous substances.

The Mercury-Steam Binary-Vapor Heat Engine

The average temperature at which heat is received may be made to approach very closely to the metallurgical limit if the working fluid is mercury, because it may be vaporized at that limit and because heating of the liquid at lower temperatures may be accomplished regeneratively. But if mercury were to be expanded in an engine until its temperature was reduced to atmospheric temperature (say 70 F) its pressure would be about 6×10^{-5} in. Hg abs, and its volume would be about 1,000,000 cu ft/lb. Then the work required to remove non-condensable gases from the condenser would be extremely high, and the cost of the great casings necessary to enclose the condenser and the low-pressure stages of the turbine would be prohibitive.

It is possible, however, to expand the mercury in an engine until some moderately low pressure is reached and then to condense it by transferring heat to water. In this process the water may be vaporized at a pressure corresponding to a temperature slightly less than that at which the mercury condenses. If the mercury is condensed at a pressure of 2 in. Hg abs, which corresponds to a temperature of 457 F, steam may be generated at any pressure up to 450 lb/sq in. abs. Then the steam may be expanded through an engine until its temperature is reduced nearly to atmospheric temperature where its pressure is not unduly low.

The relation between the rate of flow of mercury and the rate of flow of water through their respective systems is determined by the quantities of heat required for condensation in the one case and vaporization in the other. For each pound of mercury condensed at a pressure of 2 in. Hg abs the heat flow must be about 127 Btu, while for each pound of water vaporized at 450 lb/sq in. abs the heat flow must be about 757 Btu. Therefore about 6 pounds of mercury will be condensed for each pound of water vaporized.

The temperature-entropy chart of Fig. 107 shows a cycle imposed on a cycle for 1 pound of steam: it shows graphically the gain in efficiency that can be realized by the binary-fluid cycle over any Rankine cycle.

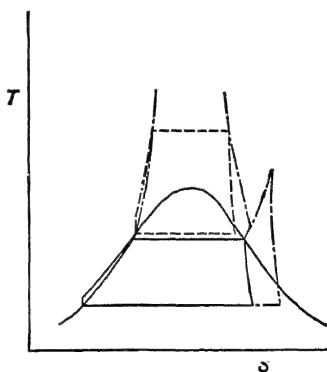


FIG. 107. Mercury-Steam Cycle

The mercury-steam cycle has been developed over a period of years by the General Electric Company, and several power plants of this type are now in operation in the United States. Published data on one of them* indicate a thermal efficiency of the heat engine of more than 35 per cent, which corresponds to a fuel consumption approximately 20 per cent less than that of contemporaneous steam plants. However, the problems encountered in making the binary-fluid plant safe, dependable, and, in view of fixed charges, economical are formidable; and equipment of this type is not at present for sale.

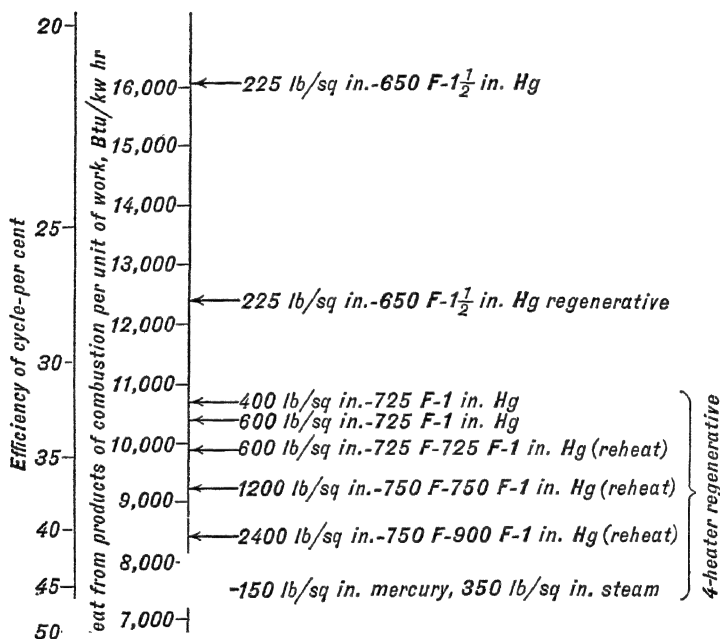


FIG. 108. Relative Performance of Power Plant Cycles
Approximate values for modern plants at best load.

Comparison of Cycles

Various power-plant cycles are compared in Fig. 108. The values given there are only approximate, but they serve to show the order and relative magnitudes of the efficiencies.

* James Orr, *Power*, July 1, 1930. He gives 10,220 Btu of heating value of fuel per kw-hr. Assuming 90 per cent for the efficiency of the boiler plant, we get for the efficiency of the heat engine 37 per cent.

Heat and Work as By-Products

The discussion of regenerative heating of feed water in the preceding section makes it evident that, *whenever heat is to be supplied at a temperature lower than that at which steam is being generated, it should come from steam which has been reduced in temperature in an engine.* This principle may be applied to any heating operation, whether it be the heating of feed water or of such widely different things as living quarters or materials employed in an industrial process.

Steam turbines may be purchased in the market which are so designed that steam may be withdrawn for heating purposes at one or several points in the course of its expansion. They are called *extraction turbines*.

If steam is being generated primarily for the production of power, then the heat it delivers may be considered a by-product. Following the usual practice in accounting, we would charge against the heating operation only the excess of cost over that when power is produced but no heat. This is equivalent to charging against heat a fraction of the cost which is proportional to the amount of additional work that could have been obtained from the steam used for heating but which was not obtained because of the heating operation.

It follows that, if heat be considered a by-product, the charge for heat will diminish rapidly with the temperature at which steam is withdrawn from the engine. For, if heating were to be accomplished at the temperature of the condenser into which the engine exhausts, the charge would vanish.

On the other hand, if steam is being generated primarily for the production of heat, then the work it delivers in a turbine through which it flows on its way to the heating process may be considered a by-product. Then we would charge against the work produced only the excess of cost over that when heat is produced but no work. It can be seen from the energy equation of steady flow [6] that this is equivalent to charging costs against heat and work in proportion to the magnitudes of the heat and work when they are expressed in the same units.* This would result in a charge against work for fuel of approximately one-quarter of the corresponding charge in a central-station power plant. For this reason an industrial plant can sometimes produce power at a cost that is less than the market price, despite the fact that its equipment is smaller and, therefore, less efficient than that of the central-station power plant. There are a few instances in the United States of the sale of power as a by-product of an industry which produces heat in large quantities.

* This is the energy (or enthalpy) method of allocating costs. The preceding method, in which heat was considered the by-product, is the availability (or *b*-function) method. (See Chapter XVII).

PROBLEMS

1. A perfect reciprocating engine constitutes part of a power plant which operates on the Rankine cycle (reversible). The boiler pressure is 200 lb/sq in. abs, and the condenser pressure is 15 lb/sq in. abs. The temperature of the steam leaving the boiler plant is 500 F. Determine:

- (a) The heat transferred to each pound of H_2O in the boiler-superheater plant.
- (b) The heat rejected to the circulating water in the condenser by each pound of H_2O .
- (c) The quality of the steam approaching the condenser.
- (d) The work area under the expansion line of the engine indicator card per pound of flow steam.
- (e) The net engine work per pound of flow steam.
- (f) The thermal efficiency of the heat engine.
- (g) The steam rate of the engine (the number of pounds of steam per horsepower-hour of work).

2. Answer all the above questions except (d) for a power plant with the same steam condition and condenser pressure but with an engine whose efficiency is 70 per cent.

3. A steam cycle has a thermal efficiency of 12 per cent. Steam is generated at 150 lb/sq in. abs and 450 F and is expanded through a reciprocating engine to a condenser in which the pressure is 5 lb/sq in. abs. Condensate leaves the condenser in the saturated liquid condition.

Answer questions (a), (b), (c), (e), and (g) of problem 1 for this case. Compute the efficiency of the reciprocating engine.

4. From the data given in Table 4 of the *Steam Tables* compute the work required to compress liquid water isentropically to 5000 lb/sq in. abs from saturation states ranging from 1 in. Hg abs to the critical state. Plot the work as ordinate against the saturation pressure as abscissa.

5. The Rankine Cycle. Plot engine work per pound of steam, ratio of feed pump work to engine work, heat added in boiler plant per pound of steam, and efficiency, of the Rankine cycle against the independent variable in each of the following cases:

- (a) Initial pressure, 250 lb/sq in. abs.
Initial temperature, 800 F.
Condenser pressure (variable), $\frac{1}{2}$ in. abs to 20 lb/sq in. abs.
- (b) Initial pressure, 250 lb/sq in. abs.
Initial temperature (variable), saturation to 1000 F.
Condenser pressure, 1 in. abs.
- (c) Initial pressure (variable), 14.7 to 3500 lb/sq in. abs.
Initial temperature, 800 F.
Condenser pressure, 1 in. abs.

6. The Reheat Cycle. Given a maximum steam temperature of 750 F and a maximum final moisture of 10 per cent, plot against boiler pressures ranging from 100 to 3000 lb/sq in. abs the thermal efficiency of otherwise perfect power plants containing turbines of 80 per cent efficiency and condensers which maintain 1 in. Hg abs pressure. When reheat is used maintain the final moisture at 10 per cent.

Find the ratio of the lowest fuel consumption with reheat to the lowest fuel consumption without reheat for the same work output.

7. Steam enters a turbine at 310 lb/sq in. abs and 700 F, and exhausts at $1\frac{1}{2}$ in. Hg abs. Assume isentropic expansion throughout and negligible leaving loss. Feed water is heated in a single open heater* which is supplied with steam from a stage of the turbine. The pressure in the heater is the same as that of the stage from which steam is extracted, and the temperature of liquid leaving the heater is identical with the saturation temperature corresponding to the pressure in the extraction stage. The condensate leaving the condenser is in the saturated state. Determine, for pressures in the extraction stage of 100, 50, 20, and 10 lb/sq in. abs:

- (a) The percentage of the possible temperature rise† that occurs in the heater.
- (b) Percentage of flow entering the turbine that is extracted.
- (c) Power from cycle for a steam flow of 1 lb/sec entering the turbine.
- (d) Power from a corresponding cycle without extraction for the same flow.
- (e) Percentage reduction in power due to extraction.
- (f) Heat supplied (Btu) per unit of work produced (kw-hr) in the extraction cycle.
- (g) Heat supplied (Btu) per unit of work produced (kw-hr) in the cycle without extraction.
- (h) Percentage saving due to extraction.

8. Steam is supplied to a certain turbine at a rate of 100,000 lb/hr. Its temperature is 700 F, and its pressure 310 lb/sq in. abs. The condenser pressure is $1\frac{1}{2}$ in. Hg abs. Steam is extracted from a single stage and delivered to a closed feed-water heater. Assume the following: overall efficiency of the turbine, 83 per cent; efficiency of that part of the turbine between the inlet and the extraction stage, 80 per cent; pressure drop between extraction stage and heater, 5 per cent of pressure in the stage; condensate leaves the condenser and the heater in the saturated state; feed water leaves the heater 5 degrees cooler than the condensate; the condensate from the heater is pumped into the feed line between the heater and the boiler; pitch diameter of last-stage wheel, 55 in.; length of last-stage bucket, 15 in.; direction of flow from last-stage buckets is axial for all conditions. Determine for a pressure in the extraction stage of 50 lb/sq in. abs the quantities (a) to (h) of the preceding problem and the following in addition:

- (i) The leaving loss in Btu/kw-hr when extracting.
- (j) The leaving loss in Btu/kw-hr when not extracting.

9. Explain why the following statement is true:

If fuel costs are charged against heat and work in proportion to the magnitudes of the heat and work, when they are expressed in the same units, the result is a charge against work of approximately one-quarter of the corresponding charge in a central-station power plant.

10. An industrial power plant requires 15,000 lb of dry saturated steam per hour at 280 F for heating. The condensate from the heating operation is recovered at atmospheric pressure and 205 F and returned to the boiler.

This steam may be supplied from an extraction turbine which has an efficiency of 75 per cent between the inlet and the extraction stage and the same efficiency between the extraction stage and the condenser. The turbine is to be supplied with steam at

* An open heater is one in which the extracted steam and the feed water are mixed. A closed heater is one in which they are kept separate and the heat is transferred through an intervening wall.

† Possible temperature rise = temperature in boiler — temperature in condenser.

400 lb/sq in. abs and is to exhaust to a condenser at $1\frac{1}{2}$ in. Hg abs. It must supply to the factory 900 kw of electrical power at the terminals of the generator.

Assume that 94 per cent of the power delivered by the steam to the turbine shaft is delivered at the terminals of the generator, that 11,000 Btu of heat is transferred to water in the steam generator for each pound of coal consumed, and that a ton of coal costs \$5.

(a) At what temperature must the steam be generated in order to deliver dry saturated steam at 280 F at the extraction opening?

(b) How much steam must be supplied at the turbine inlet to meet the power and heating demands?

(c) What would be the fuel charge per hour?

(d) What would be the fuel charge per hour if only the demand for heat were met?

(e) What would be the fuel charge per hour if only the demand for power were met?

(f) Considering power as a by-product find the cost of each kilowatt-hour of work and each Btu of heat.

(g) Considering heat as a by-product, find the corresponding costs of work and heat.

SYMBOLS

c_p	specific heat at constant pressure
E	internal energy of system in general
h	enthalpy per unit mass
p	pressure
q	a positive number representing a quantity of heat
Q	heat to system
s	entropy per unit mass
S	entropy of system
T	absolute temperature
v	specific volume
V	volume
W	work
y	mass of fluid passing out of extraction stage while unit mass enters turbine

SUBSCRIPTS

c	liquid stream passing through heater
e	fluid extracted from stage
g	steam generator
l	liquid
s	steam
t	turbine

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CHAPTER XIII

MIXTURES OF GASES AND VAPORS

The Gibbs-Dalton Law

Systems are often encountered which are mixtures of various pure substances. If a mixture remains homogeneous in composition throughout a process it may itself be considered a pure substance during that process. The properties of a particular mixture may be determined by experiment; but in the absence of experiment it would be advantageous to have a means of deducing these magnitudes from data on the properties of the components of the mixture. Again, if one of the components separates out into a separate phase (as when liquid water is formed on cooling moist air) it would be advantageous to have a means of deducing the properties of the phases in equilibrium with each other in terms of properties of the components. Such means have been found* for mixtures of real gases at low pressures only, but they can be deduced for mixtures of perfect gases in general.

Since thermodynamics is the science of work and heat, its applications must be limited to systems with boundaries† which exclude all things not of the system. Therefore, in order to relate the properties of a pure substance to those of a mixture of which it is a component it is necessary to consider the mixture and the pure substance separately.

Dalton enunciated the principle that *any gas is as a vacuum to any other gas mixed with it*. Later Gibbs restated the principle in a more general and more useful form which is known as the *Gibbs-Dalton Law*. From this law the following rules can be deduced (as shown in Chapter XXVI) for equilibrium between the components of a mixture.

1. *The pressure of a mixture of gases is the sum of the pressures of its components when each occupies alone the volume of the mixture at the temperature of the mixture.*

2. *The internal energy and the entropy of a mixture are respectively equal to the sums of the internal energies and the entropies of its components when each occupies alone the volume of the mixture at the temperature of the mixture.*

* See Chapter XX.

† See page 14.

These two rules cannot be derived from the First and Second Laws alone and, therefore, are not true for all systems comprising mixtures of gases. It is a matter of experience, however, that they hold at low pressures to a high degree of precision and that they apply to real gases over a wider range of pressures than do the relations of the perfect gas.

We may state these rules algebraically, using symbols without subscripts to denote properties of the mixture and symbols with subscripts 1, 2, \dots , n to denote respectively the properties of the separate components. Then when the various components exist separately under conditions such that

$$T = T_1 = T_2 = \dots T_n \quad [83]$$

and

$$mw \quad m_1v_1 = m_2v_2 = \dots m_nv_n, \quad [84]$$

$m = m_1 + m_2 + \dots + m_n$ $mV = V$ T, p, u, h, s	$p = p_1 + p_2 + \dots + p_n$ $\frac{1}{v} = \frac{1}{v_1} + \frac{1}{v_2} + \dots + \frac{1}{v_n}$ $mu = m_1u_1 + m_2u_2 + \dots + m_nu_n$ $mh = m_1h_1 + m_2h_2 + \dots + m_nh_n$ $ms = m_1s_1 + m_2s_2 + \dots + m_ns_n$
--	---

m_1 $m_1v_1 = V$ T, p_1, u_1, h_1, s_1
m_2 $m_2v_2 = V$ T, p_2, u_2, h_2, s_2
\vdots
m_n $m_nv_n = V$ T, p_n, u_n, h_n, s_n

FIG. 109. The Gibbs-Dalton Law

Relation between properties of mixture and properties of pure components at temperature and volume of the mixture.

where the symbol m denotes the mass of the mixture or a component, rule 1 becomes (Fig. 109)

$$p = p_1 + p_2 + \dots p_n, \quad [85]$$

and rule 2 becomes

$$mu = m_1u_1 + m_2u_2 + \cdots m_nu_n \quad [86]$$

and

$$ms = m_1s_1 + m_2s_2 + \cdots m_ns_n. \quad [87]$$

From [84], [85], and [86] we may derive an expression for the enthalpy of the mixture:

$$mh = m(u + pv) = mu + pmv$$

or

$$mh = m_1h_1 + m_2h_2 + \cdots m_nh_n. \quad [88]$$

The pressures $p_1, p_2, \cdots p_n$ in [85] are called the *partial pressures* of the components of the mixture. They are sometimes considered to be the pressures exerted by the individual components *in the mixture*. This concept cannot, of course, be verified by any thermodynamic experiment, because the pressure of a part of a system which cannot be considered a system separate from the remainder cannot be measured.

Mixtures of Perfect Gases

It was shown on page 95 that the equation of state of all pure gases at very low pressures is given by the expression

$$pv = RT,$$

where v denotes the volume of one mole of the gas and R the universal gas constant. Therefore we may write equations of the form

$$p_1v_1 = RT_1, \quad p_2v_2 = RT_2, \quad \text{etc.}, \quad [89]$$

for the various components of a mixture each in the pure form. When these gases conform to the condition [83] the right-hand members of [89] become identical. Solving each for pressure and adding them together we get

$$\sum p_i = RT \sum \left(\frac{1}{v_i} \right),$$

where \sum denotes a summation of values of the quantity for all the pure gases, that is, for $i = 1, 2, \cdots n$. Now $(1/v_i)$ is the molal density of the pure gas i which is the same as the number of moles of gas i in unit volume of the mixture. Therefore, $\sum (1/v_i)$ is the *molal density of the mixture* or the number of moles of all components per unit volume of the mixture. By [85], $\sum p_i$ is the pressure of the mixture. Therefore, we may write

$$p = \frac{RT}{v}$$

or, alternatively,

$$p = (\sum n_i) \frac{RT}{V}, \quad [90]$$

where v denotes the volume of the mixture per mole of its components, and V the total volume of a mixture consisting of $\sum n_i$ moles of component gases. Thus it is shown that a mixture of perfect gases that conforms to the Gibbs-Dalton Law is itself a perfect gas if in the equation of state which defines a perfect gas the volume of a molecular weight is replaced by the volume per mole of components. Atmospheric air may be considered to be a perfect gas at ordinary pressures and temperatures because it is a mixture of gases each of which may be considered a perfect gas.

If we define the *molecular weight of the mixture* M as the mass per mole of its components, then

$$v = Mv$$

and, by [90],

$$pv = \frac{R}{M} T, \quad [91]$$

where (R/M) is the gas constant for the mixture. *The mole fraction x_1 of substance 1 in the mixture is defined as the ratio of the number of moles of that component in a given volume of mixture to the total number of moles of all the components in that volume; thus*

$$x_i = \frac{n_i}{\sum n_i}, \quad \text{where } n_i = \frac{m_i}{M_i}. \quad [92]$$

It follows that the mass of mixture per mole of its components is given by the equation

$$M = \sum x_i M_i. \quad [93]$$

The mole fraction of substance 1 in a mixture is equal to the ratio of the partial pressure of substance 1 to the pressure of the mixture. This can be readily proved as follows: From [92], [89], and [90] respectively, we get

$$x_1 = \frac{v}{v_1}, \quad v_1 = \frac{RT}{p_1}, \quad \text{and} \quad v = \frac{RT}{p}.$$

Substituting the latter two into the first, we get

$$x_1 = \frac{p_1}{p}. \quad [94]$$

Proportions by Volume

If the mass of gas 1 which is comprised in a mixture of gases of pressure p , temperature T , and volume V is placed in a separate container and brought to the pressure and temperature of the mixture, its volume,

V'_1 , is given, according to [89], by

$$V'_1 = V \frac{p_1}{p}. \quad [95]$$

If a corresponding mass of each of the other components is similarly brought to the pressure and temperature of the mixture, the sum of all these separate volumes is the volume of the mixture (Fig. 110); thus, by [85],

$$\sum V'_i = \frac{V}{p} \sum p_i = V. \quad [96]$$

$m = m_1 + m_2 + \dots + m_n$ $\frac{m}{p}$ $V = V'_1 + V'_2 + \dots + V'_n$
--

The ratio V'_1/V is called the *part by volume of gas 1 in the mixture*. By [95] we may write for the part by volume

$$\frac{V'_1}{V} = \frac{p_1}{p}$$

m_1	m_2		m_n
T	T	T
p	p		p
V'_1	V'_2		V'_n

FIG. 110. Parts by Volume

that is, the part by volume of a component in a mixture of perfect gases is equal to the ratio of the partial pressure of the component to the pressure of the mixture. Moreover, by [94], the part by volume is identical with the mole fraction, thus,

$$\frac{V'_1}{V} = x_1. \quad [97]$$

Avogadro's Law states that at given pressure and temperature a mole of any perfect (low-pressure) gas occupies the same volume as a mole of any other perfect gas. Therefore, the volume occupied by a mass of gas at a given pressure and temperature is proportional to the number of moles and independent of the nature of the gas. Thus the ratio of the parts by volume of two components of a mixture is

$$\frac{V'_1}{V'_2} = \frac{m_1/M_1}{m_2/M_2}. \quad [98]$$

It follows that the parts by mass are related to the parts by volume in this fashion,

$$\frac{m_1}{m_2} = \frac{V'_1 M_1}{V'_2 M_2} \quad [99]$$

Specific Heats of a Mixture

The specific heats at constant volume and at constant pressure for a mixture which conforms to the Gibbs-Dalton Law are found by differen-

tiating the expressions for the internal energy and the enthalpy, [86] and [88], respectively. They are

$$c_v = \frac{1}{m} (m_1 c_{v1} + m_2 c_{v2} \cdots + m_n c_{vn})$$

and

$$c_p = \frac{1}{m} (m_1 c_{p1} + m_2 c_{p2} \cdots + m_n c_{pn}),$$

[100]

where c_{v1} and c_{p1} denote the specific heats at constant volume and pressure respectively of a unit mass of the pure gas 1 when it occupies the same volume at the same temperature as in the mixture, etc., and c_v and c_p denote the specific heats of unit mass of the mixture.

EXAMPLE. Let us use the equations deduced above to determine the relationships between the properties of air in terms of the properties of its component gases. First let us assume that air is composed of oxygen and nitrogen in the proportions by mass of 0.245 and 0.755.* Then the ratio of the parts by volume is given by [98], thus:

$$\frac{V'_O}{V'_N} = \frac{0.245/32}{0.755/28.016} = 0.284,$$

where subscripts O and N refer to oxygen and nitrogen respectively. The part by volume of oxygen is then

$$\frac{V'_O}{V'_N + V'_O} = \frac{1}{1 + V'_N/V'_O} = 0.221,$$

and the part by volume of nitrogen is 0.779. The mole fraction of oxygen is identical with its part by volume. Therefore, by [93], the "molecular weight" of air is

$$M_a = 0.221 \times 32 + 0.779 \times 28.016 = 28.90 \text{ g},$$

and its gas constant is

$$R_a = \frac{R}{M_a} = \frac{1545.4}{28.90} = 53.5.$$

The specific heats for air may be found from [100]. The following tabulation gives the specific heats of the components and the corresponding values computed for air:

	c_v	c_p
Oxygen	0.155	0.217
Nitrogen	0.177	0.248
Air	0.172	0.240

* The results of this assumption are no better than the assumption itself. The figures given on page 96 for the properties of air are more accurate because they are based on a more complete list of the components of air.

Using the perfect-gas relations of page 101 we may express the internal energy, enthalpy, and entropy of air in terms of its specific heats. We obtain a similar result if we first formulate expressions for these properties for each of the components and combine them in accordance with [86], [87], and [88].

Mixing Perfect Gases

From [96] we learn that masses m_1 , m_2 , etc. of the perfect gases 1, 2, etc., can occupy a given volume either as a mixture or as separate gases (separated by impermeable partitions) at a temperature T while exerting pressure p on the boundaries (Fig. 110).

Now the internal energy of the mixture is, by [86], the sum of the internal energies of the separate masses m_1 , m_2 , etc. at temperature T when each occupies the same volume as the mixture. However, it was shown on page 98 that the internal energy of a perfect gas is a function of temperature only and is therefore independent of volume. Consequently, the internal energy of mass m_1 of gas 1 is the same at temperature T whether it occupies a volume as large as the volume of the mixture or as small as that at which its pressure is equal to the pressure of the mixture. It follows from [86] that the internal energy of the system of n perfect gases at temperature T is the same whether they are separate or mixed.

Now if the partitions between the separate gases 1, 2, \dots n are removed and the gases are allowed to mix at constant temperature no change in internal energy will occur. Moreover, by [2], no heat will transfer because the work of the process is zero. Therefore, *if a number of perfect gases for which the Gibbs-Dalton Law holds are allowed to mix adiabatically without change in total volume from an initial state in which the gases are separately at uniform pressure and temperature, the final pressure and temperature of the mixture will be respectively the same as the pressure and temperature of the gases before mixing.*

Though the mixing process just described results in no change in internal energy, enthalpy, temperature, or pressure on the walls, it is accompanied by a marked increase in entropy. The entropy of the mixture is the sum of the entropies of the constituents when each exists alone at the temperature and the *volume* of the mixture. The volume of the mixture is in each case greater than the volume of the pure component before the mixing process occurs (Fig. 110). The entropy of the mixture may be computed from the relation [32] for the perfect gas and from the Gibbs-Dalton relation [87].

Equilibrium of a Mixture of Perfect Gases with a Pure Liquid

Another consequence of the Gibbs-Dalton Law may be stated as follows: *When a mixture of gases at low pressure is in equilibrium with a*

pure liquid, the mass of the vapor of the liquid per unit volume of mixture is the same as the density of pure vapor in equilibrium with that liquid at the same temperature.

It follows that if a mixture of gases 1, 2, \dots n is in equilibrium with the pure liquid phase of substance 1 (Fig. 111), the properties of the mixture are given by the equations

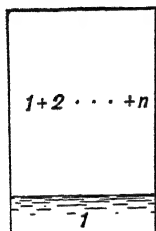


FIG. 111

and

$$p = p_{g1} + p_2 \dots + p_n, \quad [101]$$

$$\frac{1}{v} = \frac{1}{v_{g1}} + \frac{1}{v_2} + \frac{1}{v_n},$$

$$mu = m_1u_{g1} + m_2u_2 \dots + m_nu_n, \quad [102]$$

$$mh = m_1h_{g1} + m_2h_2 \dots + m_nh_n,$$

$$ms = m_1s_{g1} + m_2s_2 \dots + m_ns_n,$$

where subscript $g1$ refers to the saturated state of vapor of substance 1 at the temperature of the mixture.

Specific Humidity, Relative Humidity, and Dew Point

The science which deals with the behavior of mixtures of air* and water vapor is called hygrometry or psychrometry. We shall employ three terms from its vocabulary:

The *specific humidity* ω is the ratio of the mass of water vapor in a given volume of mixture to the mass of air in the same volume.

The *relative humidity* ϕ of a mixture is the ratio of the mass of water vapor in unit volume of mixture to the density of saturated water vapor at the temperature of the mixture. When the relative humidity is 1 the mixture is said to be *saturated*.

The *dew point* of a mixture is the temperature to which the mixture must be cooled at constant pressure before liquid water will form.

From the first definition we get

$$\omega = \frac{m_s}{m_a} = \frac{v_a}{v_s}, \quad [103]$$

* Here and in subsequent paragraphs the term air is used to denote the usual mixture of gases which constitute the atmosphere, exclusive of water vapor. Such a mixture is sometimes called *dry air*. This distinction between water vapor and the other constituent gases arises because, first, the amount of water vapor contained in a given mass of air is extremely variable compared with the amounts of the other constituents, and, second, water vapor alone among the constituents can often be condensed out in a separate phase without unusual changes in temperature or volume.

where subscripts s and a denote water vapor and air respectively. Introducing the perfect gas relation we get

$$\omega = \frac{M_s p_s}{M_a p_a} = 0.622 \frac{p_s}{p_a} \quad [104]$$

where M_s and M_a denote the molecular weights of water and air — the term molecular weight being applied to air in the sense used on page 204.

The definition of relative humidity may be written in the form

$$\phi = \frac{v_g}{v_s}, \quad [105]$$

where v_g denotes the specific volume of saturated water vapor at the temperature of the mixture. Again using the perfect-gas relation, we find

$$\phi = \frac{p_s}{p_g}, \quad [106]$$

where p_g is the saturation pressure of water at the temperature of the mixture. Combining [103] and [105], we get

$$\phi = \omega \frac{v_g}{v_a}, \quad [107]$$

and from [104] and [106]

$$\phi = \frac{\omega}{0.622} \frac{p_a}{p_g}. \quad [108]$$

Moreover, by the Gibbs-Dalton Law, the pressure of the atmosphere p is given by

$$p = p_a + p_s,$$

which by [104] or [106] can be expressed in terms of ω or ϕ .

The determination of the dew point involves a process in which the pressure of the mixture remains constant. To interpret the dew-point temperature in terms of the characteristics of water vapor it is necessary to know the course of the partial pressure of the water vapor during the process. We may write for water vapor in the mixture

$$p_s = \frac{R_s T}{v_s},$$

and for the mixture

$$p = \frac{R_m T}{v},$$

where R_m denotes the gas constant of the mixture. Then

$$\begin{aligned}\frac{p_s}{p} &= \frac{R_s v}{R_m v_s} \\ &= \left(\frac{R_s}{R_m}\right) \left(\frac{m_s}{m}\right),\end{aligned}\quad [109]$$

where m_s and m are masses of water vapor and mixture in a given volume. It follows that the partial pressure of the water vapor remains unchanged as long as the pressure and the composition of the mixture remain unchanged.

When liquid begins to form as a result of cooling at constant pressure, then the temperature is at the dew point, and, by [101], the partial pressure of the water vapor is the saturation pressure corresponding to the dew point (Fig. 112). But this is also the partial pressure of the water vapor before cooling. Therefore *the partial pressure of water vapor in a mixture is the saturation pressure corresponding to the dew point.*

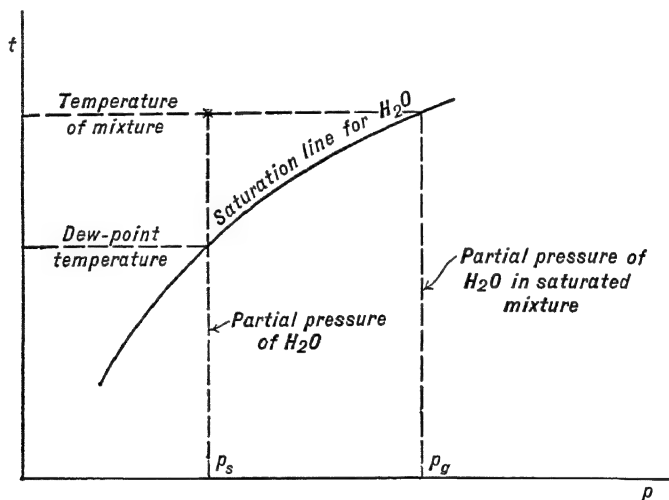


FIG. 112

The proportions of air and water vapor can be found from a measurement of the dew-point temperature through [109]. But a more common means of measurement is the psychrometer or wet-and-dry-bulb thermometer. It comprises two thermometers, one of which is covered by a wick which is thoroughly wetted by water. When the two thermometers are exposed to a stream of moist air the dry one will indicate the temperature of the mixture and the wet one will indicate the temperature of the liquid in the wick. Unless the air is "sat-

urated" with water vapor the partial pressure of the water vapor in the mixture will be too low for equilibrium with the liquid, and the liquid will evaporate. Evaporation without transfer of heat results in a drop in temperature of the liquid which in turn results in transfer of heat from mixture to liquid of increasing magnitude with increasing drop in temperature.

For true equilibrium both the surface of the liquid and the mixture around it must fall in temperature to the dew point; but transfer of heat from the stream of mixture will raise the temperature of the liquid to a value somewhere between the dew point and the temperature of the mixture when a steady state is reached. This temperature of the steady state is called the *wet-bulb temperature*. The difference between the temperature of the mixture and the wet-bulb temperature is a

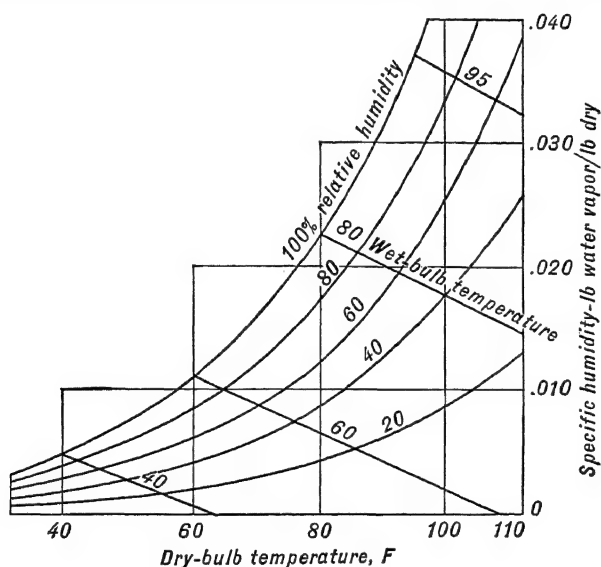


FIG. 113. Psychrometric Chart

measure of the amount of water vapor in the mixture, for when the difference vanishes, the mixture and the liquid are in equilibrium, the mixture is saturated, and the temperature of the mixture, the wet-bulb temperature, and the dew point are identical. The relation between the moisture content of the mixture, the temperature, and the wet-bulb temperature has been determined experimentally. It is shown in Fig. 113 for a mixture under a pressure of 1 standard atmosphere.*

* For a more detailed chart see Macintire, *Refrigeration Engineering*, Wiley, 1940, p. 294.

EXAMPLE. To illustrate all that has gone before let us consider a mixture of air and water vapor which is 3.45 per cent water vapor by volume at a pressure of 1 standard atmosphere and at a temperature of 100 F.

By [97] the mole fraction is identical with the part by volume, so that

$$x_s = 0.0345;$$

also, by [95], the ratio of the partial pressure of the water vapor to the pressure of the mixture is the same value: thus

$$\frac{p_s}{p} = 0.0345,$$

$$p_s = 0.0345 \times 14.696 = 0.507 \text{ lb/sq in.}$$

and

$$p_a = 14.696 - 0.507 = 14.189 \text{ lb/sq in.}$$

The specific humidity can be found from [104], thus:

$$\omega = 0.622 \times \frac{0.507}{14.189} = 0.02223.$$

At 100 F the saturation pressure is found from the *Steam Tables* to be

$$p_g = 0.9492 \text{ lb/sq in.}$$

Then the relative humidity is given by [106] as

$$\phi = \frac{0.507}{0.9492} = 0.5345.$$

The dew point t_d is the temperature for which the saturation pressure is 0.507 lb/sq in. The *Steam Tables* give

$$t_d = 80 \text{ F.}$$

Now let us find the thermodynamic properties of the mixture. By [86] to [88] the internal energy, enthalpy, and entropy of the mixture are respectively the sums of the internal energies, enthalpies, and entropies of the two components when each occupies the volume of the mixture alone at the temperature of the mixture. The density of the mixture (the mass in unit volume) is obviously the sum of the densities of the two components when each occupies the volume of the mixture alone.

The values for the internal energy, enthalpy, and entropy of the mixture each depend upon two arbitrary constants which are determined when a state is chosen for each of the two components at which the value of the property is zero. If we let the constants for water vapor be fixed by the *Steam Tables* we may take values of the properties from the *Steam Tables* without modification.

The specific volume of the water vapor may be found most readily from the

perfect-gas equation, which is adequate at low pressures:

$$\begin{aligned}v_s &= \frac{85.78T}{144p_s} \\ &= 657.6 \text{ ft}^3/\text{lb.}\end{aligned}$$

By extrapolation in the *Steam Tables* it is easy to find values for internal energy and enthalpy: thus

$$\begin{aligned}u_s &= 1043.6 \text{ Btu/lb.} \\ h_s &= 1105.2 \text{ Btu/lb.}\end{aligned}$$

The entropy for this state cannot be taken directly from the *Steam Tables*, but both the equation for the change in entropy of a perfect gas [31] and equation [16a] of Keenan and Keyes indicate that a good approximation to the change in entropy at constant temperature is given by

$$s_2 - s_1 = R \ln \frac{p_1}{p_2}$$

at low pressures. Evaluating this equation between the saturated vapor state and the state corresponding to a pressure of 0.507 lb/sq in., both at a temperature of 100 F, we get

$$\begin{aligned}s_s &= 1.9826 + \frac{85.78}{778.3} \ln \frac{0.9492}{0.507} \\ &= 2.0517 \text{ Btu/lb degree F.}\end{aligned}$$

The specific volume of air may be found from the perfect-gas equation

$$v_a = \frac{R_a T}{p_a}$$

if R_a is evaluated in accordance with [18a]. Using a suitable value the specific volume becomes

$$\begin{aligned}v_a &= \frac{53.35T}{144p_a} \\ &= 14.61 \text{ ft}^3/\text{lb.}\end{aligned}$$

In evaluating the internal energy and entropy we shall arbitrarily make their values zero at one standard atmosphere and 0 F. Then, by [22a]

$$u_a = c_v t = 0.171t = 17.1 \text{ Btu/lb,}$$

and

$$h_a = c_v t + pv = c_v t + R_a T = 55.46 \text{ Btu/lb.}$$

For the entropy we use [32], thus:

$$s_a = 0.240 \ln \left(\frac{t + 459.7}{459.7} \right) + \frac{53.35}{778.3} \ln \frac{14.696}{14.189} = 0.04973 \text{ Btu/lb degree F.}$$

It is now possible to compute the properties of the mixture by the summations of [85] to [88]. The following table summarizes the results:

TABLE II

Substance	Pressure lb/in. ²	Specific volume ft ³ /lb	Internal energy Btu/lb	Enthalpy Btu/lb	Entropy Btu/lb F
Water vapor	0.507	657.6	1043.6	1105.2	2.0517
Air	14.189	14.61	17.1	55.46	0.04973
Mixture	14.696	14.29	39.42	78.29	0.09322

In the analysis of a process the arbitrary constants do not appear, because only differences between properties are employed. For example, let us calculate the heat transferred while moisture is removed from the mixture just analyzed as it is cooled at constant pressure to 70 F. At this temperature the maximum possible* partial pressure of the water vapor is, by the *Steam Tables*,

$$p_g = 0.3631 \text{ lb/sq in.}$$

Then the maximum specific humidity is

$$\omega = 0.622 \times \frac{0.3631}{14.696 - 0.3631} = 0.01576.$$

For each pound of air being cooled the amount of liquid formed is equal to the decrease in the specific humidity. Therefore, in its final state, the system consists of 0.01576 lb of water vapor and $(0.02223 - 0.01576)$ or 0.00647 lb of liquid water for each pound of air.

By the First Law the heat received by the system in this process at constant pressure is equal to its increase in enthalpy. Using single and double accents to denote initial and final states respectively, we may write for the heat received by the system

$$Q = m''h'' + m_l'h_l' - m'h',$$

where subscript l denotes the liquid phase. By virtue of [88] we may write

$$\begin{aligned} Q &= m_a''h_a'' + m_s''h_s'' + m_l'h_l' - m_a'h_a' - m_s'h_s' \\ &= m_a(h_a'' - h_a') + m_s''h_s'' + m_l'h_l' - m_s'h_s', \end{aligned}$$

or for the heat per unit mass of air (not mixture)

$$\frac{Q}{m_a} = h_a'' - h_a' + \left(\frac{m_s''}{m_a}\right)h_s'' + \left(\frac{m_l'}{m_a}\right)h_l' - \left(\frac{m_s'}{m_a}\right)h_s'.$$

* Here reference is made to stable states only. It is shown on page 429 that metastable states may persist for which the partial pressure of water vapor may be higher than the saturation pressure.

The change in the enthalpy of air at constant pressure (and, in fact, in general) can be represented, by [22a], as

$$h_a'' - h_a' = c_p(T_a'' - T_a').$$

Moreover the values of $h_s'' + h_l'$ are identical with h_g and h_f respectively at the final temperature, and h_s' is given above. Substituting these values we get

$$\frac{Q}{m_a} = -14.31 \text{ Btu/lb of air,}$$

the sign indicating that heat flows from the system.

It is permissible to use an expression of the form

$$h_s'' - h_s' = c_p(t'' - t')$$

to find the change in enthalpy of water vapor at low pressures. A satisfactory value for c_p below 100 F is 0.45 Btu/lb F. However, when some of the vapor condenses it is necessary to employ the *Steam Tables*, so that little economy of effort results from the use of the specific heat.

The Reversible Adiabatic Process

Once the method of computing properties of mixtures is learned, the usual applications of the First and Second Laws to changes in the state of the mixture are easily made. The reversible adiabatic, or isentropic, process is of particular interest.

The isentropic condition for a mixture of two components may be stated in accordance with [87] in the form

$$m_1 ds_1 + m_2 ds_2 = 0, \quad [110]$$

provided that the quantity of neither component is changed in the process. Now the change in entropy of a perfect gas is given by

$$ds_1 = c_{p1} \frac{dT}{T} - R_1 \frac{dp_1}{p_1} = c_{p1} \frac{dT}{T} - \frac{v_1}{T} dp_1$$

so that [110] becomes

$$(m_1 c_{p1} + m_2 c_{p2}) \frac{dT}{T} - \frac{V}{T} (dp_1 + dp_2) = 0. \quad [111]$$

By virtue of the perfect-gas equation we may write for each of the components an equation of the sort

$$p_1 = \frac{m_1 R_1 T}{V},$$

so that

$$p_2 = \frac{m_2 R_2}{m_1 R_1} p_1$$

and
$$dp_2 = \frac{m_2 R_2}{m_1 R_1} dp_1.$$

Substitution of this expression in [111] gives

$$\left(1 + \frac{m_2 c_{p2}}{m_1 c_{p1}}\right) m_1 c_{p1} \frac{dT}{T} - \left(1 + \frac{m_2 R_2}{m_1 R_1}\right) \frac{V}{T} dp_1 = 0. \quad [112]$$

Now, if $\frac{m_2 c_{p2}}{m_1 c_{p1}} = \frac{m_2 R_2}{m_1 R_1}$, [112] reduces to

$$m_1 c_{p1} \frac{dT}{T} - \frac{V}{T} dp_1 = 0$$

or

$$ds_1 = 0,$$

and the change in state of component 1 (and therefore of component 2) as it follows the states marked by the volume and temperature of the mixture is isentropic. This is true when

$$\frac{c_{p2}}{R_2} = \frac{c_{p1}}{R_1},$$

or when

$$k_2 = k_1.$$

The components of air, nitrogen, and oxygen, have approximately equal values of k , so that in any isentropic process the change in entropy of each component as it follows the course of the volume and temperature of the mixture is zero.

On the other hand the value of k for water vapor is about 1.3 whereas for air it is about 1.4; so that the entropy of water vapor, in states corresponding to states of a mixture, changes while the entropy of the mixture remains unchanged. We shall determine the direction of the change of entropy of water vapor. Since

$$\frac{c_p}{R} = \frac{k}{k-1},$$

it follows that when

$$k_s < k_a$$

then

$$\left(\frac{c_p}{R}\right)_s > \left(\frac{c_p}{R}\right)_a$$

and

$$\frac{m_s c_{ps}}{m_a c_{pa}} > \frac{m_s R_s}{m_a R_a}$$

Moreover,

$$1 + \frac{m_s c_{ps}}{m_a c_{pa}} > 1 + \frac{m_s R_s}{m_a R_a}.$$

so that, by [112],

$$m_a c_{pa} \frac{dT}{T} < \frac{V}{T} dp_a.$$

Consequently, for isentropic compression

$$ds_a < 0.$$

It also follows from [110] that

$$ds_s > 0.$$

It would therefore be erroneous to assume, for example, that in an isentropic expansion of moist air to the condensation point the entropy of saturated vapor at the condensation pressure would be the same as the entropy of water vapor at the initial volume and temperature of the mixture.

Steady Flow of Mixtures of Air and Water Vapor

Many processes employed by the engineer involve a change in state of a mixture of air and water vapor in the course of steady flow through an apparatus. The processes that occur in an air compressor, a heater, a humidifier, and a cooling tower are examples. The fluid may enter as a mixture of air and water with a parallel stream of liquid water, as in the last two examples. It may leave as a single stream or as several streams.

In order to apply the First Law to problems of this sort we shall first expand [5a] to the form

$$\sum_1 w \left(h + \frac{V^2}{2g} + z \right) = \sum_2 w \left(h + \frac{V^2}{2g} + z \right) - Q + W_x, \quad [113]$$

where \sum_1 denotes a summation over all the streams entering the apparatus (Fig. 114), \sum_2 a summation over all the streams leaving, w the mass rate of flow in a single stream where it enters or where it leaves, and Q and W_x respectively heat entering the apparatus and work leaving along a shaft in unit time.

If two streams enter the apparatus, one being a mixture of air and water vapor and the other being liquid

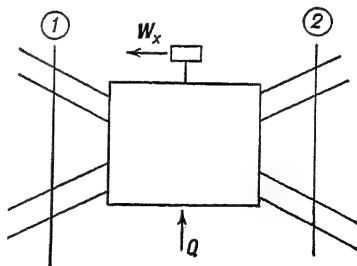


FIG. 114

water, the left-hand member of [113] may be expanded as follows:

$$w_1 h_1 + w_{l1} h_{l1} + w_1 \left(\frac{V_1^2}{2g} + z_1 \right) + w_{l1} \left(\frac{V_{l1}^2}{2g} + z_{l1} \right);$$

where subscript 1 refers to the mixture of air and water vapor entering and subscript *l1* refers to the liquid entering. A similar group of terms may be found for the right-hand member. The quantity h_1 may in turn be expanded in accordance with [88], thus:

$$w_1 h_1 = w_{s1} h_{s1} + w_{a1} h_{a1},$$

where w_{s1} and w_{a1} are respectively the masses of water vapor and air entering the apparatus per unit time in the stream of mixture and h_{s1} and h_{a1} are respectively the enthalpies per unit mass of water vapor and air when each is at the same temperature and occupies the same volume as the mixture that contains it. It can readily be seen that for purposes of analysis the air and water vapor may each be considered a separate stream having the temperature, velocity, and position of the stream of mixture and having each a pressure equal to its corresponding partial pressure in the mixture.

For steady flow the mass of air entering in a given time must equal the mass of air leaving in that time. Moreover, the total mass of water vapor and liquid water entering in a given time must equal the total mass of water vapor and liquid leaving in that time. Therefore we may write as further conditions that must be satisfied the following:

$$\begin{aligned} m_{a1} &= m_{a2}, \\ m_{s1} + m_{l1} &= m_{s2} + m_{l2}. \end{aligned} \tag{114}$$

PROBLEMS

In the following problems the pressures referred to are absolute pressures.

1. A homogeneous mixture of perfect gases 1, 2, \dots , n , with masses m_1, m_2, \dots, m_n , exists at pressure p and temperature T . The energy and entropy for each gas existing separately are arbitrarily set at zero when the individual gas is at p_0 and T_0 . For the mixture at p and T , find expressions for:

- (a) The internal energy.
- (b) The enthalpy.
- (c) The entropy.

2. A mixture of perfect gases at 20 lb/sq in. and 75 F consists of 1 lb of H_2 and 1 lb of N_2 . The energy and entropy for each gas existing separately are arbitrarily set at zero when the pressure and temperature of the individual gas are respectively 14.7 lb/sq in. and 32 F. Find for each constituent: (a) the partial pressure, and (b) the part by volume. Find for the mixture: (c) the volume, (d) the internal energy, (e) the enthalpy, (f) the entropy, (g) the specific heat at constant volume, (h) the specific heat at constant pressure, and (i) the isentropic exponent k .

3. Consider the mixture in the preceding problem to consist of one pound mole of H_2 and one pound mole of N_2 , and find the quantities (a) to (i).

Consider it to consist of equal parts H_2 and N_2 by volume and find the quantities (a) to (i).

4. A mixture consisting of 2 lb of helium and 1 lb of hydrogen at 20 lb/sq in. and 100 F is compressed reversibly and adiabatically to 100 lb/sq in. Find the following quantities corresponding to the final state of the mixture (let the internal energy and entropy of the separate gases be zero at 32 F and 14.7 lb/sq in.): (a) partial pressure of helium, (b) temperature, (c) internal energy of the mixture, (d) enthalpy of the mixture, (e) work done by the mixture, (f) entropy of the helium at the final temperature and volume of the mixture.

For comparison with (f) find the entropy of the helium at the initial temperature and volume of the mixture.

5. Perfect gases 1, 2, \dots n exist separately (between impermeable membranes) in an insulated chamber. Each gas is at pressure p_0 and temperature T_0 . The partitions are removed and the gases are allowed to mix, until a homogeneous mixture is present. Considering all the gases taken together as the system, find:

(a) The change in internal energy.

(b) The change in enthalpy.

(c) The change of entropy in terms of the universal gas constant and the mole fractions of the n components.

6. A rigid, insulated chamber is divided in two by an impermeable partition. On one side a pound mole of O_2 exists at pressure p_0 and temperature T_0 , and on the other side a pound mole of N_2 exists at the same pressure and temperature. The partition is removed and the gases mix thoroughly. For the system comprising both components, find the change in:

(a) Internal energy.

(b) Enthalpy.

(c) Entropy.

7. A rigid, insulated chamber is divided in two by an impermeable partition. One side contains two pound moles of CO_2 and the other side contains three pound moles of CO_2 , both at the same pressure p_0 and temperature T_0 . The partition is removed, and a homogeneous mixture results. For the system comprising 5 moles of CO_2 , find the change in:

(a) Internal energy.

(b) Enthalpy.

(c) Entropy.

8. In each of the following problems the system consists of 1 lb of nitrogen and 2 lb of water vapor. Initially these two gases are separated by a movable but impermeable diaphragm which is a good enough conductor of heat to insure temperature equilibrium between the two gases in the initial state. The initial pressure is 1000 psia and the initial temperature 560 F.

In each problem the process consists of the mixing of the gases as a result of destruction of the diaphragm. Properties of nitrogen may be found from the relations for a perfect gas; those of water vapor must be found from the *Steam Tables*. It may be assumed that the Gibbs-Dalton Law holds for the mixture.

In the following tabulation the symbols Δt , Δp , etc. denote algebraic increases in the properties temperature, pressure, etc. Each column represents a separate problem for which the zeros in the column indicate the restraints.

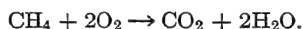
Fill in the blank spaces in the tabulation with numbers.

Process	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
Δt	0	0			
Δp		0		0	0
ΔV	0		0	0	
ΔS					
Q			0		0
W					

9. A certain gas mixture is composed of 30 per cent CO_2 , 50 per cent O_2 , and 20 per cent N_2 by mass. The mixture is initially at 70 F and 17.0 lb/sq in. After passing through a heat exchanger in steady flow the mixture is at 110 F and 14.7 lb/sq in. Find the change of entropy per pound of mixture, and the heat transferred per pound of mixture.

10. During the power stroke of an internal-combustion engine, the products of combustion are composed of 80 per cent N_2 , 15 per cent CO_2 , 3 per cent O_2 , and 2 per cent H_2O by mass. At a certain point of the stroke the temperature is 500 F, the pressure is 150 lb/sq in., and the volume is 0.10 cu ft. A short time later the temperature is 300 F and the pressure is 80 lb/sq in. Analysis of an indicator card for this period shows that the gases do 1100 ft-lb of work on the piston. Find the heat transfer during this time.

11. Methane (mol. wt. 16) is burned at constant pressure with just enough oxygen to permit complete combustion. The equation of the reaction is



If the temperature and pressure of the final mixture are 90 F and 14.7 lb/sq in. respectively:

- Find the partial pressure of water vapor in the products of combustion.
- Find the number of pounds of liquid water in the products of combustion per pound of methane.
- Find the volume of the products of combustion per pound of fuel, neglecting the volume of liquid water.

12. Solve problem 11, assuming that the oxygen for combustion is obtained by using atmospheric air whose composition is 21 per cent O_2 and 79 per cent N_2 by volume.

13. The Weather Bureau records for a certain date indicate a temperature of 82 F, barometric pressure of 29.60 in. Hg, and a relative humidity of 75 per cent. Find:

- The partial pressure of the water vapor.
- The partial pressure of the air.
- The specific humidity.
- The dew point.
- The density of the mixture.

14. To determine the effect of moisture content on the density of the atmosphere, find the density of a mixture of air and water vapor at 70 F and 14.70 lb/sq in. if the relative humidity is (a) zero, (b) 0.50 and (c) unity. What are the dew-point temperatures for these three conditions?

15. The temperature of the windows in a house on a day in winter is 40 F. If the temperature in the room is 72 F, and the barometer is 29.48 in. Hg, what would be the maximum relative humidity that could be maintained in the room without condensation on the window panes?

16. Forty pounds per minute of a mixture of air and water vapor at 14.70 lb/sq in., 85 F, and 75 per cent relative humidity enter a mixing chamber, and there mix adiabatically with 10 lb/min of a mixture of air and water vapor at 14.70 lb/sq in., 40 F, and 30 per cent relative humidity. The fluid leaving the chamber is at 14.40 lb/sq in. Determine the temperature and the specific and relative humidities of the mixture leaving the chamber.

17. A fan discharges 10,000 cu ft of moist air per minute at 95 F, 15.30 lb/sq in., and 92 per cent relative humidity.

(a) What is the specific humidity of the mixture?

(b) Determine the number of pounds of water vapor and of "dry air" passing through the fan per minute.

18. The mixture of air and water vapor of the preceding problem is passed over refrigerator coils in steady flow (in order to dehumidify it) and is exhausted from the refrigerator chamber with a pressure and temperature of 14.6 lb/sq in. and 45 F respectively. The temperature of the condensate leaving the chamber is 45 F.

(a) What is the final specific humidity of the mixture?

(b) Determine the mass of water condensing on the coils per unit time.

(c) What is the heat transfer per unit time to the refrigerating coils?

19. One pound of a mixture of air and water vapor at 70 F, 14.70 lb/sq in., and 75 per cent relative humidity is confined in a cylinder behind a leakproof, frictionless piston. The mixture is compressed at constant temperature until the pressure is 29.40 lb/sq in.

(a) What are the final relative and specific humidities?

(b) Determine the number of pounds of liquid water precipitated.

(c) Find the work and heat for the process.

20. Atmospheric air is compressed and stored in a tank having a capacity of 5 cu ft. The conditions in the tank shortly after it is charged are as follows: temperature 120 F, pressure 80 lb/sq in., relative humidity 20 per cent. At the time the air is to be used, it is found that the temperature is 90 F. For the final state, find the specific and relative humidities, and the pressure. Also find the work and heat during the time that the temperature dropped from 120 F to 90 F.

21. An air-tight refrigerator room, with a volume of 1500 cu ft, contains initially a mixture of air and water vapor at 80 F and 15.0 lb/sq in., with a relative humidity of 80 per cent. A short time after the refrigerating apparatus is set in operation, the temperature in the room is 40 F.

(a) Find the temperature at which liquid water first forms.

(b) Find the partial pressure of water vapor in the final mixture.

(c) Find the partial pressure of air in the final mixture (neglect the volume of liquid water).

(d) Find the number of pounds of liquid water precipitated.

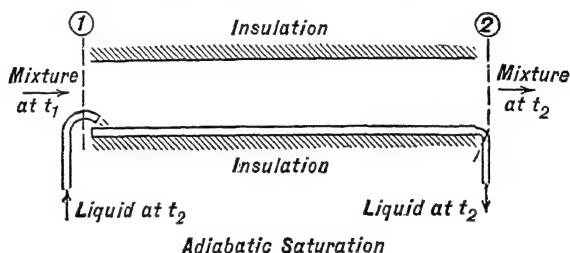
(e) Find the work and heat during the process, for the system which comprises the initial mixture.

22. Two thousand cubic feet of an air-water vapor mixture at 14.70 lb/sq in. and 55 F, with a relative humidity of 80 per cent, enters each minute a heating chamber in which the temperature of the air is raised to 75 F at constant pressure.

(a) What is the final relative humidity of the air?

(b) Determine the heat transfer from the heating coils to the mixture.

(c) Find the change in entropy per pound of mixture.



23. If a mixture of air and water vapor is passed in steady flow and without change in pressure through a long duct one wall of which consists of a surface of liquid water, the mixture will leave in a saturated state and at the temperature of the liquid with which it is in contact. The temperature at which the mixture leaves the duct is called the *temperature of adiabatic saturation*, provided only that the liquid water is introduced at this same temperature. As regards mixtures of air and water vapor, the temperature of adiabatic saturation is almost identical with the wet-bulb temperature. This identity is not maintained if the liquid is anything other than water.

Derive an expression for the specific humidity, ω_1 , of the mixture entering the duct in terms of the properties of air, water vapor, and liquid water, and the specific humidity of the saturated mixture leaving the duct.

24. A mixture of air and water vapor at 14.70 lb/sq in. and 80 F has a specific humidity of 0.013 lb vapor per lb air. Find the temperature of adiabatic saturation for this mixture. Compare this temperature with the wet-bulb temperature for the mixture (the psychrometric chart gives 69.4 F for the wet-bulb temperature).

25. A mixture of air and water vapor at 14.70 lb/sq in. and 80 F is passed through an adiabatic saturation apparatus. The temperature of the mixture leaving the apparatus is 60 F. Find the specific and relative humidities for the original mixture.

26. The dehumidification of a mixture of air and water vapor without large reductions in temperature is often accomplished by passing the mixture over refrigerating coils and heating coils placed in series. In the refrigerating chamber the temperature of the mixture is reduced (with consequent condensation of water vapor) until the desired specific humidity is obtained. In the heating chamber the temperature is raised to the desired value. The entire process is at essentially constant pressure.

It is desired to change 20,000 cu ft of mixture per minute from a temperature of 80 F and relative humidity of 96 per cent to a temperature of 70 F and relative

humidity of 50 per cent, in the apparatus described. The barometer is 30 in. Hg. The condensate leaves the refrigerating chamber at 40 F.

(a) Find the mass of water vapor condensing per unit time in the refrigerating chamber.

(b) Find the heat transfers per unit time to the refrigerating and heating coils.

27. An air-washer comprises a chamber into which a water spray is introduced and from which the liquid water is removed at the bottom of the chamber. A mixture of air and water vapor is passed through the spray and dust particles and foreign odors are removed. The mixture leaving the spray is saturated, or nearly so. The moisture content of the mixture may be raised or lowered, depending on whether the temperature of the spray is above or below the dew point of the original mixture. The process occurs adiabatically at essentially constant pressure.

Five thousand cubic feet per minute of a mixture of air and water vapor at a temperature of 65 F and pressure of 14.70 lb/sq in. with a relative humidity of 70 per cent enters an air-washer, and leaves as a saturated mixture at 60 F. Water is supplied to the chamber at a temperature of 70 F at the rate of 30 lb/min. Determine the temperature at which the water leaves the chamber.

28. A cooling tower is to be designed for the following conditions:

Temperature of water entering	= 120 F
Temperature of water leaving	= 90 F
Temperature of air entering	= 75 F
Relative humidity of air entering	= 70 per cent
Temperature of air leaving	= 100 F
Relative humidity of air leaving	= 100 per cent.

Five thousand pounds of water per minute are to enter the tower. Determine the number of cubic feet of air per minute entering the tower at standard atmospheric pressure. Also, find the number of pounds of make-up water required per minute.

29. Atmospheric air at 14.60 lb/sq in., 60 F, and 55 per cent relative humidity passes through the suction duct of a forced-draft centrifugal fan on a cooling tower at the rate of 3000 cfm. The power input to the fan is 5 horsepower. The mixture of air and water vapor leaves the tower saturated at 90 F. The temperature of the water entering the tower is 115 F, and 180 lb of water per minute leave the tower. Determine the exit temperature of the water and the rate at which water is supplied to the tower.

SYMBOLS

c_p	specific heat at constant pressure
c_v	specific heat at constant volume
g	acceleration given to unit mass by unit force
h	enthalpy per unit mass
k	c_p/c_v for a perfect gas
m	mass
M	mass of mixture, molecular weight
p	pressure
Q	heat to system
R	gas constant

R	universal gas constant
s	entropy per unit mass
S	entropy
t	temperature (Fahrenheit)
t_d	dew-point temperature
T	absolute temperature
u	internal energy of unit system in the absence of motion, gravity, etc.
v	specific volume
v	volume per mole
V	volume
w	mass rate of flow
x	mole fraction
z	height

GREEK LETTERS

ϕ	relative humidity
ω	specific humidity

SUBSCRIPTS

a	air
g	saturated state of vapor
l	liquid phase
m	mixture
s	water vapor

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CHAPTER XIV

INTRODUCTION TO THE THERMODYNAMICS OF CHEMISTRY

Application of the First Law to Chemical Reactions

The purpose of this chapter is not to develop the thermodynamics of chemistry toward extensive practical applications, but rather to show the essential unity of all thermodynamic reasoning by deriving some of the basic relations and concepts of chemistry from the same statements of the First and Second Laws that have served so well the study of systems in which no chemical reactions occur. The practicing chemist must build on this foundation an elaborate structure some of whose members are empirical relations that are approximations to true relations. Approximation must often suffice either because of ignorance of the true relations or because simple relations are necessary to mathematical analysis.

In the thermodynamics of chemistry we depart from a consideration of the pure substance alone to deal with systems which are not necessarily homogeneous in either composition or state and the parts of which may vary in composition in the course of a process.

The behavior of such non-homogeneous systems can best be studied in terms of the homogeneous subsystems which they comprise. A subsystem which is homogeneous in composition and state is called, after Gibbs, a *phase* of the system. Thus, a system consisting of gaseous air and solid carbon comprises two phases, the air and the carbon. After the carbon is burned and the product of combustion has diffused through the surrounding material, a single phase may exist consisting of a homogeneous gaseous mixture of oxygen, nitrogen, and carbon dioxide.

For any change of state in any system we may write

$$dQ = dE + dW. \quad [2]$$

We shall limit our discussion for the present to those changes of state which can be carried out without the aid of electricity or magnetism and without involving capillary forces, gravity, or appreciable motion. Then for E we may substitute U .*

* This substitution implies a somewhat broader interpretation of the symbol U than was given in Chapter III, where it was employed to denote the internal energy of a pure substance in the absence of motion, gravity, etc. In this chapter it denotes the internal energy of any system in the absence of motion, gravity, etc. In Chapter III the quantity U is a function of two independent properties only — here it is dependent on the state of chemical aggregation as well. However, in both instances it is independent of velocity, position in the gravitational field, etc.

If a change of state occurs while the system is confined in a rigid container, the work may be zero, or

$$dW = 0;$$

then [2] becomes

$$dQ = dU$$

for each step in the process. Upon integrating we get

$$Q = U_2 - U_1, \quad [115]$$

where subscripts 1 and 2 refer respectively to the initial and final states. For example, if the system consists of oxygen and carbon initially, and carbon dioxide finally, then U_1 is the sum of the internal energies of the carbon and oxygen in the initial state and U_2 is the internal energy of the carbon dioxide in the final state. Of course, U_1 and U_2 must be reckoned from the same reference state of the carbon-oxygen system. We might, for instance, arbitrarily make the value of the internal energy of carbon zero at 1 atmosphere and 70 F and do the same with oxygen. Then U_1 is the increase in energy of the carbon-oxygen system in going from 1 atmosphere and 70 F to the initial state, and U_2 is the increase in going from the same reference condition to the combined form at the final pressure and temperature.

If the change of state occurs at constant pressure under the restraint of a piston which receives or delivers the only work involved in the process, then [2] becomes

$$dQ = dU + d(pV) = dH,$$

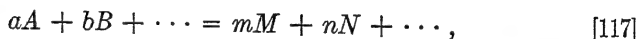
since $d(pV)$ is the work done. Integration results in the expression for the heat received by the system:

$$Q = H_2 - H_1, \quad [116]$$

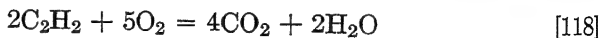
where H_2 denotes the final enthalpy of the system and H_1 the initial enthalpy.

Heats of Reaction

The science of chemistry teaches that when a chemical reaction occurs the reactants combine in certain definite proportions to form certain products in definite proportions. This fact is stated in a *chemical equation* which is of the form



where A , B , etc., denote units of the reactants; M , N , etc., units of the products; and a , b , \cdots , m , n , \cdots numbers. For example, the equation



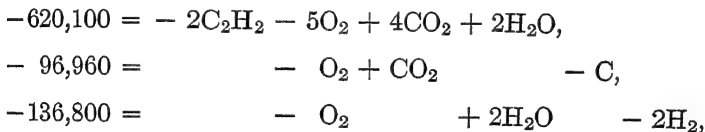
indicates that two moles of acetylene combine with five moles of oxygen to form four moles of carbon dioxide and two moles of water. If a system consisting of the reactants A , B , etc., each constituting a separate phase and each present in the proportions given by the chemical equation [117], is allowed to change its state at constant volume until only the products M , N , etc., remain, each in a separate phase, then the heat received by the system during the process is the difference between the internal energy of the products and that of the reactants. We may write

$$Q = -aA - bB - \cdots + mM + nN + \cdots, \quad [119]$$

if A , B , M , N , etc., each denotes now the *internal energy* of one mole of its corresponding substance in the state in which it exists at the beginning or end of the process. If the initial and final temperatures are the same, then $(-Q)$ is known as the *constant-volume heat of reaction* — the minus sign being a consequence of a difference between the conventions of chemistry and thermodynamics.

The same heat equation [119] will serve for a process at constant pressure if we interpret A , B , M , etc., each as the *enthalpy* of one mole of its corresponding substance. If the initial and final temperatures are the same, then $(-Q)$ is known as the *constant-pressure heat of reaction*; or, if the pressure and temperature have the normal values for the laboratory, $(-Q)$ is often referred to as the *heat of reaction* without qualification.

In the calculation of heats of reaction at constant pressure the enthalpy of each chemical element at the pressure and temperature in question is usually taken to be zero. Then the heat of formation of a compound is the negative of its enthalpy. A more general method of analysis which sometimes is precisely equivalent to the previous one consists of the reduction of several linear equations of the type [119] into a desired form. For example, from the following three equations,



it can be shown that the heat of formation of acetylene is $-47,730$ calories per mole, or

$$47,730 = \text{C}_2\text{H}_2 - 2\text{C} - \text{H}_2,$$

for, to get this result, it is only necessary to multiply the second equation through by 4 and subtract it and the third equation from the first.

The usefulness of the analysis given above, the results of which are included in [119] and its interpretations, would be seriously limited by

the requirement that the component substances A , B , M , etc., must appear only as separate phases, were it not that failure to satisfy this requirement often does not introduce appreciable error. For example, a system comprising hydrogen and oxygen, both initially in the vapor phase and ready to combine, would be a single gaseous phase unless a very special mechanism were provided to keep all parts of both gases separate until the moment of combination. But since the internal energy and the enthalpy of most mixtures of vapors at low pressures are known to be very closely equal to the sums of the corresponding values found for the constituent vapors alone at the temperature of the mixture,* the statement [119] can often be applied to mixtures without modification.

The rate of change of the heat of reaction with temperature can be found by differentiating [116]:

$$\frac{dQ}{dt} = \frac{dH_2}{dt} - \frac{dH_1}{dt} = C_2 - C_1,$$

where C_2 and C_1 are respectively the specific heats at constant pressure of the products and the reactants. Evidently

$$C_1 = ac_A + bc_B + \cdots$$

and

$$C_2 = mc_M + nc_N + \cdots,$$

where $c_A, \cdots c_M, \cdots$ each denotes a specific heat at constant pressure for a unit (mole or gram) of a reactant or a product.

Application of the First Law to Solutions

For a change of state in a solution we may write

$$Q = U_2 - U_1 \quad [115]$$

if the volume remains constant, and

$$Q = H_2 - H_1 \quad [116]$$

if the pressure remains constant, for the same reasons (and within the same limitations) as those stated for a chemical reaction (page 226). In fact, chemical reactions often occur between solutes in a given solvent while reactants and products remain in the dissolved state. Then the value of U or of H in the above equations must be that of the entire system — the solvent included. Thermodynamics can never assign a value to U (or, in consequence, to H) for a part of a system which cannot in itself be considered a separate system with boundaries exclud-

* See Chapter XIII.

ing all other matter, for it is only from measurements of work and heat, which are boundary phenomena, that internal energy can be evaluated.

In chemistry much importance is attached to the behavior of extremely dilute solutions, as, for example, the reaction between dilute hydrochloric acid and dilute sodium hydroxide. The internal energy or specific volume of a unit mass of either of these solutions would differ so slightly from the same values for the pure solvent that only by carrying a number of significant figures unwarranted by the precision to which the quantity is known could the difference be made to appear.

This difficulty is avoided by means of the "partial" property, which is defined by the expression

$$\bar{s}_1 = \left(\frac{\partial P}{\partial m_1} \right)_{t, p, m_2, m_3, \dots} \quad [120]$$

where P is a property of the system comprising masses m_1, m_2 , etc., of substances 1, 2, etc., and \bar{P}_1 is the corresponding partial property of substance 1 in the system. For example, the partial volume of sodium chloride, in an aqueous solution of sodium chloride, is the rate of increase in the volume of the solution with respect to its content of sodium chloride at constant temperature, pressure, and mass of solvent: thus

$$\bar{V}_2 = \left(\frac{\partial V}{\partial m_2} \right)_{t, p, m_1},$$

where subscript 2 refers to the salt and subscript 1 to the water. The quantity \bar{V}_2 may be thought of as a differential coefficient, or as the increase in volume of an infinitely large amount of solution when unit mass of solute is added at constant pressure and temperature.

As an example of the use of a partial property we shall derive an expression for the heat of solution at constant temperature and pressure

of a salt in an aqueous solution of that salt. Consider a mass of solution and an elementary mass of the solute dm_2 to constitute a system (Fig. 115). The enthalpy of the system in this initial state is $(H + h_s dm_2)$, where H denotes the enthalpy of the solution and h_s the enthalpy of unit mass of the solid solute. If the solid is added to the solution and allowed to dissolve at constant pressure and temperature, the final enthalpy of the system will be $(H + \bar{H}_2 dm_2)$; and the increase in

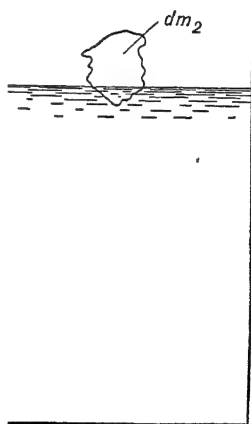


FIG. 115

enthalpy of the system between initial and final states will be

$$(\bar{H}_2 - h_s) dm_2.$$

By [116] this is the heat received by the system during the process. The heat of solution is, therefore,

$$-dQ = (h_s - \bar{H}_2) dm_2. \quad [121]$$

Since the term "heat of solution" is understood to refer to the process of solution at constant temperature, the quantities h_s and \bar{H}_2 must refer to the same temperature as well as to the same pressure.

If the amount of solute added is finite the heat of solution can be stated in terms of the integral of [121]:

$$-Q = h_s(m_2'' - m_2') - \int_{m_2'}^{m_2''} \bar{H}_2 dm_2,$$

where m_2' denotes the initial amount of solute in solution and m_2'' the final amount. (An alternative expression for $-Q$ which includes no unresolved integral is given by [127] below.)

Basic Relations Involving Partial Properties

Any system which is heterogeneous in composition and state may be considered to consist of a number of *phases*, each of which is homogeneous in composition and state. If the system experiences a change of state, matter may transfer from one phase to another. Thus the state of a phase may be altered by a change in its composition as well as by a change in its pressure and temperature. If it is uninfluenced by motion, gravity, capillarity, electricity, or magnetism, the value of a property P for the phase may be expressed in the form

$$P = f(p, t, m_1, m_2, \dots), \quad [122]$$

where P denotes the property in question, f a functional relation, p the pressure by which the phase is constrained, t the temperature at which it is maintained, and m_1, m_2 , etc., the masses of substances 1, 2, etc., which it comprises.

This point of view implies that a phase is to be considered an *open system* — that is, a system whose boundaries are penetrable to matter as well as to work and heat. It should be remembered that the First Law cannot be applied directly to such a system.* Nevertheless we can without reference to the First Law derive certain relations between the properties of such a system and the corresponding partial properties. When either of the Laws of Thermodynamics are to be applied, we shall employ only closed systems.

* See footnote, page 33.

We may write for the change in any property P of a phase during a small change of state

$$dP = \left(\frac{\partial P}{\partial p}\right)_{t, m_1, m_2 \dots} dp + \left(\frac{\partial P}{\partial t}\right)_{p, m_1, m_2 \dots} dt + \left(\frac{\partial P}{\partial m_1}\right)_{p, t, m_2 \dots} dm_1 + \quad [123]$$

which is a differential statement of [122]. If the change of state occurs at constant pressure and temperature [123] simplifies to

$$dP = \frac{\partial P}{\partial m_1} dm_1 + \frac{\partial P}{\partial m_2} dm_2 + \dots,$$

or, by virtue of the definition [120] of a partial property,

$$dP = \bar{P}_1 dm_1 + \bar{P}_2 dm_2 + \dots \quad [124]$$

The magnitude of any partial property corresponding to the definition [120] is dependent on the pressure, temperature, and relative composition of the phase and not on its size. To verify this statement, consider two homogeneous systems at the same temperature and pressure and having identical relative compositions, in the first of which the mass of each component is twice that in the second. If we add a mass dm_1 of substance 1 to the first system at constant pressure and temperature, the increase in volume, for instance, will be twice that of the second system when it receives the mass $\frac{1}{2}dm_1$ of the same substance, for the second system reproduces the behavior of the first at one-half scale. The ratio of the increase in volume to the mass added is the same in each instance. Therefore the partial volumes of substance 1 in the two systems are identical. Similar reasoning will result in the same conclusion concerning any other partial property.

A system of any composition may be increased in size *without change in its composition* by adding masses dm_1 , dm_2 , etc., of substances 1, 2, etc., if dm_1 , dm_2 , etc., bear the same relation to each other as do the masses of these substances that are already present in the system, that is, if

$$dm_1 : dm_2 = m_1 : m_2$$

In this fashion a system may be built up at constant pressure, temperature, and relative composition from a total mass of zero to any desired finite total mass. To each step of this process we may apply the general equation for the change in a property:

$$dP = \bar{P}_1 dm_1 + \bar{P}_2 dm_2 + \quad [124]$$

Each of the partial properties, according to the principle stated above, is constant throughout the process. Therefore, upon integration we find the value of the property to be related to the values of the partial prop-

erties in the following simple way:

$$P = \bar{P}_1 m_1 + \bar{P}_2 m_2 + \dots \quad [125]$$

A relation between the partial properties which does not involve the corresponding property can be derived from [124] and [125]. From [125] we get by differentiation the statement

$$dP = \bar{P}_1 dm_1 + m_1 d\bar{P}_1 + \bar{P}_2 dm_2 + m_2 d\bar{P}_2 + \dots$$

Previously, however, it was found that

$$dP = \bar{P}_1 dm_1 + \bar{P}_2 dm_2 + \dots; \quad [124]$$

so that by subtraction we get

$$m_1 d\bar{P}_1 + m_2 d\bar{P}_2 + \dots = 0. \quad [126]$$

As an example of the use of [126] consider a two-component system, for which the relation reduces to

$$\frac{d\bar{P}_1}{d\bar{P}_2} = -\frac{m_2}{m_1}.$$

If, then, \bar{P}_1 increases with a certain change in composition, \bar{P}_2 must decrease during that change; and \bar{P}_1 is a maximum for the composition

for which \bar{P}_2 is a minimum, and vice versa (Fig. 116). For the pure solvent (that is, for $m_2 = 0$) the rate of change of \bar{P}_2 with respect to the solute is infinite if the rate of change of \bar{P}_1 is finite, and the rate of change of \bar{P}_2 can be finite only if the rate of change of \bar{P}_1 is zero.

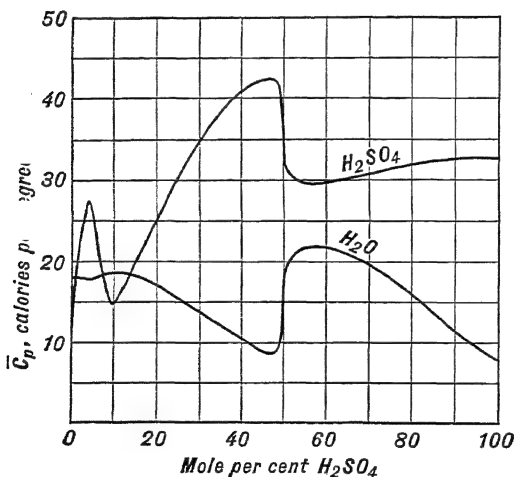


FIG. 116. Partial Molal Specific Heats of H_2O and H_2SO_4 in Aqueous Sulphuric Acid

From *Thermodynamics*, Lewis and Randall, McGraw-Hill (1923), p. 87.

Consider a system comprising two solutions of different magnitude and composition but made up of the same two component substances 1 and 2. If the two are mixed at constant pressure and temperature a new homogeneous solution is formed different in composition from either of the original solutions. The heat of the process is

$$-Q = \sum H' - H'',$$

where H'' denotes the enthalpy of the entire mass in its final state and $\sum H'$ denotes the sum of the enthalpies of the two solutions in their respective initial states. If we use subscripts 1 and 2 to refer to components 1 and 2 and subscripts a and b to refer each to one of the original solutions, then the heat of solution of a in b may, by virtue of [125], be expressed as

$$-Q = m_{1a}\bar{H}_{1a} + m_{2a}\bar{H}_{2a} + m_{1b}\bar{H}_{1b} + m_{2b}\bar{H}_{2b} - (m_{1a} + m_{1b})\bar{H}_1'' - (m_{2a} + m_{2b})\bar{H}_2''. \quad [127]$$

Relative Partial Enthalpy

It is sometimes desirable to express the value of a partial property of a solution as the excess over its value at some prescribed composition of the solution. This quantity is called a *relative* partial property. Thus, the *relative partial enthalpy*, \bar{L}_1 , of substance 1 in a solution may be defined by the equation

$$\bar{L}_1 = \bar{H}_1 - \bar{H}_1^\circ,$$

where \bar{H}_1° denotes the partial enthalpy of substance 1 in an infinitely dilute solution at the same pressure and temperature as the solution in question. Similarly, the relative partial enthalpy, \bar{L}_2 , of substance 2 in the solution is given by

$$\bar{L}_2 = \bar{H}_2 - \bar{H}_2^\circ.$$

Using the superscript \circ to refer to the infinitely dilute solution and considering substance 1 to be the solvent, we have

$$\bar{L}_1^\circ = 0, \quad \bar{L}_2^\circ = 0,$$

and

$$\bar{H}_1^\circ = h_1^\circ, \quad [128]$$

where h_1° denotes the enthalpy per unit mass of pure solvent. Moreover, it can readily be shown that the heat of solution of a mass dm_1 of solvent in a solution is given by

$$-dQ = -\bar{L}_1 dm_1,$$

and that the heat of solution of mass dm_2 of solute is given by

$$-dQ = -[\bar{L}_2 - L_2] dm_2,$$

where L_2 denotes the relative partial enthalpy of the solute in pure solute—that is, $h_2 - \bar{H}_2^\circ$. It can also be shown that the expression [127] for the heat of solution of a in b will still hold if the corresponding relative partial enthalpy is substituted for each partial enthalpy in the equation.

Chemical Reaction and Solution in Steady Flow

In the field of chemical engineering, processes are often encountered in which material in a stream of fluid reacts with or dissolves in a substance in another stream. These processes may be analyzed with the aid of [5a], which may be expressed in the expanded form

$$\sum_1 (wh) + \sum_1 \frac{wV^2}{2g} + \sum_1 (wz) = \sum_2 (wh) + \sum_2 \frac{wV^2}{2g} + \sum_2 (wz) - Q + W_x \quad [129]$$

where \sum_1 indicates a summation for all the entering streams and \sum_2 for all the leaving streams, w denotes the mass rate of flow of a stream, h its enthalpy per unit mass of fluid, V its velocity, z its height, Q the heat entering the apparatus per unit time, and W_x the shaft work leaving it per unit time. If a stream consists of a solution its enthalpy may be expressed in terms of partial enthalpies as indicated in [125]. Of course, most steady-flow processes encountered in chemical engineering may be analyzed by means of a simpler form of [129], such as

$$\sum_1 (wh) = \sum_2 (wh) - Q.$$

Applications of the Second Law

Consider a heterogeneous system in temperature equilibrium with a large surrounding medium (a constant-temperature bath). For each step in a change of state occurring in the system we may write by [2]

$$dW = dQ - dE.$$

In the course of the proof of the principle of increase of entropy (Chapter VIII) it was shown that

$$dS \geq \frac{dQ}{T}. \quad [16]$$

Therefore, if we substitute $T dS$ for dQ in the expression for dW given above, we get

$$dW \leq T dS - dE.$$

Then the maximum amount of work that the system can do as it changes from a state corresponding to S and E to one corresponding to $(S + dS)$ and $(E + dE)$ is equal to

$$T dS - dE.$$

Moreover, this is the work done by the system in a reversible change from the first state to the second, because in a reversible change dQ and $T dS$ are identical.

For a process at constant temperature the maximum possible work, dW_m , may be expressed in the forms

$$dW_m = -d(E - TS) = -d\Psi,$$

where Ψ^* denotes the property $(E - TS)$. The maximum possible work corresponding to a finite change of state at constant temperature is therefore the decrease in the value of Ψ : thus,

$$W_m = \Psi_1 - \Psi_2, \quad [130]$$

where subscripts 1 and 2 refer respectively to the initial and final states.

The decrease in Ψ is not only the maximum work which the system can produce while changing at constant temperature from state 1 to state 2; it is also the maximum work which the system can produce while changing from state 1 to state 2 when no heat reservoir is used other than the constant-temperature medium. For, if a process could be found between states 1 and 2 in which the system produces work in excess of the decrease in Ψ , that process could be made part of a cycle of which a reversible change at constant temperature from 2 to 1 is the other part. This reversible change would require an amount of work $(\Psi_1 - \Psi_2)$, and the direct change would produce, by assumption, more than this amount. Therefore, work could be produced continuously at the expense of heat from the medium only. Since this conclusion contravenes the Second Law, it follows that *the maximum amount of work which a system can produce when it changes between two states in each of which it is in temperature equilibrium with the same large environment is equal to the decrease in the value of Ψ for the system.*

This maximum amount of work may be either greater or less than zero, depending on the direction of the process. When it is less than zero we can say that the minimum amount of work that must be *delivered* to the system in order to cause the change of state is equal to the increase in the value of Ψ .

For complete equilibrium with the medium the system must assume a fixed pressure as well as a fixed temperature. Then the work delivered to the medium by the system is at least

$$p(V_2 - V_1), \dagger \quad [131]$$

* Gibbs used ψ and ζ to denote the properties $(E - TS)$ and $(H - TS)$ respectively. Following present conventions, we shall use the lower case to denote the value of the property for a unit system and capitals for systems in general.

† By inducing motion within a medium further work might be transferred to it; but, if the medium is initially at rest and unable to act upon the system through electrical, gravitational, or capillary effects, then $p(V_2 - V_1)$ is the least work which can pass from system to medium.

where V_2 and V_1 denote respectively the final and initial volumes of the system and p denotes the pressure of the medium. The maximum work which can be obtained from the process for useful purposes — that is, for purposes other than displacement of the medium — is therefore

$$\Psi_1 - \Psi_2 - p(V_2 - V_1),$$

in accordance with [130] and [131]. Since p is identical with the initial and final pressures of the system, we may write for the maximum useful work of the process

$$\begin{aligned} W_u &= (\Psi_1 + p_1 V_1) - (\Psi_2 + p_2 V_2) \\ &= Z_1 - Z_2, \end{aligned} \quad [132]$$

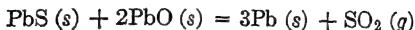
where Z denotes the property $(\Psi + pV)$ which is also $(H - TS)$. It follows that *the maximum amount of useful work which a system can produce when it changes between two states in each of which it is in temperature and pressure equilibrium with the same large environment is equal to the decrease in the value of Z for the system.* When the maximum amount of useful work is less than zero, we can say that the minimum amount of work that must be provided by things other than the surrounding medium is equal to the increase in the value of Z .

Since almost all of man's attempts to produce useful work begin with a system in pressure and temperature equilibrium with the atmosphere of the earth, and need not be abandoned until a similar equilibrium is reestablished, the foregoing principle is of great service in prescribing a limit to the usefulness of such processes. For example, the electrical work which can be produced by a lead storage cell as it discharges cannot exceed the decrease in the value of Z between the charged and discharged conditions. Similarly the work which can be delivered by a mixture of fuel and air to the flywheel of an internal-combustion engine cannot exceed the decrease in Z for the fuel-air system between its original state and that of the products of combustion at the temperature and pressure of the atmosphere. In practice the work obtained from the most efficient internal-combustion engines scarcely exceeds one-half of this maximum value, although the work obtained from a lead storage cell may reach 90 per cent of the maximum value. Further discussion of the problem of the production of work from a chemical reaction will be found in Chapter XVI.

PROBLEMS

The symbols (*s*), (*l*), and (*g*) denote solid, liquid, and gaseous states respectively.

1. Calculate the heat transfer and its direction for the reaction



at 1 atmosphere and 20 C from the following heats of formation per gram-mole for the same pressure and temperature:

PbO (*s*) 50,300 cal; PbS (*s*) 19,300 cal; SO₂ (*g*) 70,200 cal.

2. The heat of combustion at 20 C and 1 atmosphere for decane (C₁₀H₂₂) is 1613.8 kcal/g mole; for pentane (C₅H₁₂), 834.6 kcal/g mole; and for pentene (C₅H₁₀), 804.4 kcal/g mole. Estimate the heat given off when decane is cracked to form pentane and pentene.

3. Find the heat that must be transferred in forming an infinitely dilute solution of one mole of zinc chloride in water at 1 atmosphere and 20 C starting from Zn (*s*), Cl (*g*), and H₂O (*l*) at the same pressure and temperature. Use the following information for 1 atmosphere and 20 C:

Heat of formation of one gram-mole of HCl (*g*), 22,000 cal.

Heat of solution of one gram-mole of HCl (*g*) in a large quantity of water, 17,300 cal.

Heat given off = +34,200 cal in the reaction



4. The heat of combustion of carbon at constant volume to CO₂ is 94,250 cal/mole of carbon if the initial and final temperatures are both 25 C.

Find the heat of combustion at constant pressure. (Assume that the volume initially occupied by the carbon is negligible, and that the gases involved are perfect gases.)

Find the heat of combustion in steady flow and at constant pressure at 25 C.

5. The heat of combustion at constant volume of a certain oil is 17,670 Btu/lb at 20 C if no liquid is present in the products. The composition of the oil is



where *n* is a number. Find the corresponding constant-pressure heat of combustion. (Neglect the initial volume of the oil. Assume that the Gibbs-Dalton Law holds for the final mixture of gases. Assume that the gases involved are perfect gases, and that the gas constant is 1.986 Btu/lb-mole F.)

6. Assume that in a lead storage cell the reaction is



(a) Find the heat evolved while one mole of Pb is dissolved in the cell at 1 atmosphere pressure and at 18 C temperature if the change takes place while the battery is on the shelf and not connected electrically to any external device.

(b) A series of sixteen such cells is operating a 32-volt motor which delivers $\frac{1}{2}$ hp and operates at 90 per cent efficiency. Estimate the heat evolved by the batteries per horsepower-hour of work performed, assuming the temperature of the batteries to be constant at 18 C. For each gram mole of lead dissolved in one cell 193,000 coulombs (ampere-seconds) of electricity flows through the cell.

Heats of formation at 18 C and 1 atmosphere in kilocalories per gram mole are as follows:

PbO ₂	(crystalline)	65.0
H ₂ SO ₄	(liquid)	193.75
PbSO ₄	(crystalline)	218.5
H ₂ O	(liquid)	68.37

7. Justify the following statements as they appear on page 233:

$$\bar{L}_1^\circ = 0, \quad \bar{L}_2^\circ = 0, \quad \bar{H}_1^\circ = h_1^\circ,$$

$$-dQ = -\bar{L}_1 dm_1, \quad \text{and} \quad -dQ = -(\bar{L}_2 - L_2) dm_2$$

8. Justify the statement that [127] still holds if an \bar{L} is substituted for each \bar{H} .

9. By analogy with [125] let us define the *relative enthalpy* of a solution in terms of its relative partial enthalpies by the equation

$$L = m_1 \bar{L}_1 + m_2 \bar{L}_2 + \dots$$

Show that the relative enthalpy and the partial relative enthalpy are related in other respects in the same manner as any property and its corresponding partial property.

In the following table the subscripts 1 and 2 refer to water and sulphuric acid respectively, m denotes mass, and \bar{L} the relative partial enthalpy in calories per gram at 18 C and 1 atmosphere.

$m_2/(m_1 + m_2)$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.85	0.9	0.95	1
\bar{L}_1	0	-1.5	-5.5	-12	-21.5	-36	-60	-106	-187	-278	-355	-415	-455
\bar{L}_2	0	18	38	57	77	97	120	145	173	189	200	205	206

10. What is the relative enthalpy of a solution of 4 grams of sulphuric acid in 6 grams of water at 18 C?

11. Calculate the heat of solution at constant pressure and temperature (18 C) for the following cases:

(a) One gram of sulphuric acid is added to an indefinitely large mass of aqueous sulphuric acid in which the sulphuric acid is 40 per cent by weight.

(b) One gram of sulphuric acid is added to 1 gram of water.

(c) Five grams of sulphuric acid is added to 5 grams of aqueous sulphuric acid in which the sulphuric acid is originally 20 per cent by weight.

(d) Five grams of water is added to 5 grams of aqueous sulphuric acid in which the sulphuric acid is originally 20 per cent by weight.

(e) Ten grams of aqueous sulphuric acid, 20 per cent sulphuric acid by weight, is added to 40 grams of aqueous sulphuric acid which is 70 per cent sulphuric acid by weight.

12. Show by an approximate calculation that the change in the tabulated value of \bar{L}_1 between values of $m_2/(m_1 + m_2)$ of 0.7 and 0.9 is consistent with the tabulated values of \bar{L}_2 between those limits.

13. When 1 gram of sodium chloride is added at constant temperature and pressure to a large mass of sodium chloride solution containing 31 grams of water per gram of solute 15 calories of heat is taken from the surroundings. The solution in question has the following partial relative enthalpies:

$$\bar{L}_1 = 0.05 \text{ cal/g}; \quad \bar{L}_2 = -2.43 \text{ cal/g.}$$

Find the relative enthalpy of solid sodium chloride. (See problem 9.)

14. Show by reference to a pressure-volume diagram (a) that the minimum work of compression and (b) that the maximum work of expansion of air between two states at the same temperature are both given by the change in Ψ , provided that heat is exchanged only with a single reservoir whose temperature is the same as that of the air in its initial and final states. (Show how the work can be more than the minimum or less than the maximum.)

15. Show that the maximum useful work (work in addition to that necessary to displace the environment) that can be obtained by changing from saturated liquid at the pressure and temperature of the environment to saturated vapor at the same pressure and temperature is zero provided that the environment is the only heat reservoir employed by the system.

16. Steam is sometimes found to exist as a vapor at pressures higher than the saturation pressure corresponding to its temperature. Such steam is said to be supersaturated.

(a) If steam (superheated or supersaturated) at 150 F can be assumed to be an ideal gas, compute the change in enthalpy and entropy between the saturation state and a supersaturated state at the same temperature and at 10 lb/sq in. abs. Find from these changes the values of enthalpy and entropy for the supersaturated state.

(b) Find the maximum possible useful work that could be obtained in an environment at 10 lb/sq in. abs and 150 F by changing 1 lb of supersaturated steam in pressure and temperature equilibrium with the environment to liquid water in pressure and temperature equilibrium with the environment. No heat reservoir other than the environment is to be employed.

Can you devise a process by which this work could be realized?

17. If a mixture of carbon dust and oxygen in the correct proportions is burned in steady flow in a calorimeter, 14,140 Btu of heat must be transferred out per pound of carbon introduced if the stream is to enter at 77 F and to leave as pure CO_2 at 77 F. The entropy of the product of combustion at 77 F is 0.0028 Btu/F higher than the entropy of the carbon-oxygen mixture at 77 F per pound of carbon present.

How much work could be obtained at 77 F from a reversible electrolytic cell in which the sole net effect was the reaction of carbon with oxygen to form CO_2 ? (Give the quantity of work per pound of carbon consumed in the cell.) The cell is to exchange heat only with an atmosphere at 77 F.

18. (a) It is desired to separate atmospheric air into its constituents: nitrogen and oxygen. Find the minimum work that must be expended if 1 lb of air at a pressure of 1 standard atmosphere and at a temperature of 70 F is to be separated into 0.768 lb of nitrogen and 0.232 lb of oxygen at the same pressure and temperature. Assume that the Gibbs-Dalton Law holds.

(b) If the air were separated into two volumes, each equal to the original volume and each containing only one of the constituents at the original temperature, what would be the minimum amount of work necessary to bring each of these constituents to a pressure of 1 atmosphere?

(c) Compare the minimum work of (a) with that of (b). What is the minimum amount of work necessary to separate the air into two volumes, each equal to the original volume and each containing only one of the constituents at the original temperature?

19. A galvanic cell can be constructed in which a lead electrode is in contact with solid lead chloride and a mercury electrode is in contact with mercurous chloride and these electrodes are immersed in a liquid electrolyte.

If an electromotive force of 0.5357 volt is applied across the electrodes at 25 C no reaction will occur. If this electromotive force is slightly reduced the reaction



proceeds from left to right; if the electromotive force is slightly increased the reaction proceeds from right to left.

For each mole of lead that enters into combination (or that forms from the dissociation of PbCl_2), 192,988 coulombs (ampere-seconds) of electricity flows into and out of the cell. Assume for each of the processes referred to below that the temperature of the cell is 25 C initially and finally.

(a) Find the magnitude and direction of the change in Z in the above reaction per mole of lead consumed.

The enthalpy decreases by 22,730 cal/mole of lead consumed in this reaction.

(b) Find the direction and magnitude of the heat flow per mole of lead consumed when the emf is 0.5357 volt.

If a large current is allowed to flow from the cell, the internal resistance to the flow of electricity causes a decrease in the emf at the electrodes. However, the number of coulombs transported per mole of lead remains the same.

(c) Find the direction and magnitude of the flow of heat per mole of lead consumed if the emf across the electrodes is 0.4 volt.

The reaction will proceed from left to right at a slow rate if the cell is left in storage with no electrical conductor joining the two electrodes.

(d) Find the direction and magnitude of the flow of heat per mole of lead consumed in the process of deterioration in storage.

(e) Find the changes in entropy of the cell at 25 C in the processes corresponding to (b), (c), and (d).

SYMBOLS

a, b , etc.	numbers
A, B , etc.	units of reactants
c	specific heat at constant pressure per mole or gram
C	specific heat at constant pressure
E	internal energy of a system in general
h	enthalpy per unit mass
H	enthalpy
\bar{H}	partial enthalpy
\bar{L}	relative partial enthalpy
m	mass
m, n , etc.	numbers
M, N , etc.	units of products
p	pressure
P	property of system
\bar{P}	corresponding partial property

Q	heat to system
S	entropy
t	temperature
T	absolute temperature
U	internal energy of system in the absence of motion, gravity, etc.
V	volume, velocity
\bar{V}	partial volume
w	mass rate of flow of a stream
W	work
\dot{W}_s	shaft work per unit time
\dot{W}_u	useful work
z	height

GREEK LETTERS

ψ	$(u - Ts)$
Ψ	$(E - TS)$
ζ	$(h - Ts)$
Z	$(H - TS)$
Σ	summation

SUBSCRIPTS

1, 2	initial and final states respectively, component substances
m	maximum
m_1, m_2, \dots	constant mass of substance 1, substance 2, . . .
p	constant pressure
s	solid solute
t	constant temperature

SUPERScript

o	infinitely dilute solution
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CHAPTER XV

REFRIGERATION

A *refrigerating machine* is a device which operates in cycles and receives heat at one temperature and rejects heat at a higher temperature. Any reversible engine which receives heat reversibly at one temperature and rejects heat reversibly at a lower temperature will serve as a refrigerating machine when reversed. Thus, the Carnot engine has been proposed in previous discussions of the corollaries of the Second Law as a device which may be employed either as an engine or as a refrigerating machine — the idealized regenerative heat engine of page 184 would serve as well.

A Carnot cycle which is confined to states in the vapor phase has in practice two grave defects: first, the quantities of work involved in the various processes are large compared with the net work, so that small degrees of irreversibility result in large decreases in net work; second, isothermal compression and expansion can be only approximated at any reasonable rate of operation because only low rates of heat transfer can be attained. On the other hand, a Carnot cycle in a region of two-phase states is not at all impracticable. The transfer of heat at constant temperature occurs in constant-pressure processes, which are easy to realize in steady flow. Moreover, the work of compression is not greatly in excess of the net work of the cycle because the work of expansion is small.

To illustrate, a Carnot cycle in two-phase states is shown in Fig. 117 on a pressure-volume diagram and on a temperature-entropy diagram. Saturated liquid in a state a at temperature T_1 is expanded reversibly and adiabatically to state b at temperature T_2 . In steady flow the work delivered to the engine shaft in this process is the decrease in the enthalpy of the fluid, which is in turn the area $lab21$ on the pressure-volume diagram. (For we may write

$$Td s = du + p dv = dh - v dp,$$

which is equivalent to

$$dh = v dp$$

when $ds = 0$.) At the lower temperature, T_2 , heat is received by the fluid at constant pressure, as it flows along in thermal contact with the

thing to be cooled, until it reaches a state c which has the same entropy as the saturated vapor at the higher temperature T_1 . Next, the fluid is compressed at constant entropy to state d , the saturated-vapor state. The shaft work that must enter the steady-flow apparatus during this process is measured by the area $1dc21$ of the pressure-volume diagram. It is large compared with the expansion work and, consequently, of the same order of magnitude as the net flow of work to the machine. At the higher temperature, T_1 , heat is rejected by the fluid at constant pressure as it flows along in thermal contact with the heat sink.

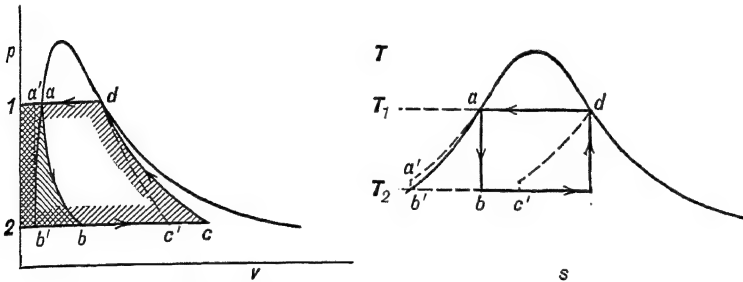


FIG. 117. Reversible Cycles in the Two-Phase Region

The reversed regenerative process is indicated in Fig. 117 by the figure labeled $a'adc'b'a'$. Since both this and the Carnot cycle are completely reversible and both receive and reject heat reversibly and isothermally, they have the same ratio of heat received to heat rejected, for the definition of the absolute scale of temperature requires that

$$\frac{q_1}{q_2} = \frac{T_1}{T_2},$$

where q_1 and q_2 are respectively the heat received and the heat rejected for either cycle. The regenerative cycle has the smaller ratio of work of compression to net work, and, therefore, it would be affected less by irreversibility; but the greater simplicity of the mechanism of the Carnot machine more than offsets this advantage.

Heat engines are commonly used to produce work for a large number of services or operations each of which consumes a relatively small portion of the work from the engine; that is, engines are, in general, relatively large central devices which meet the power demands of anything from a small factory to a large state. Refrigerating machines are usually much smaller devices, because their product is of more limited application. Thus the net work employed in a refrigerating cycle is generally small. The positive work of the cycle (for example, area

1ab21 of Fig. 117) is even smaller, and it is for this reason that the positive work is seldom large enough to justify economically the cost of the equipment necessary to obtain it.

The alternative is to drop the temperature from T_1 to T_2 by an irreversible expansion through a throttle valve. In Fig. 118 the cycle

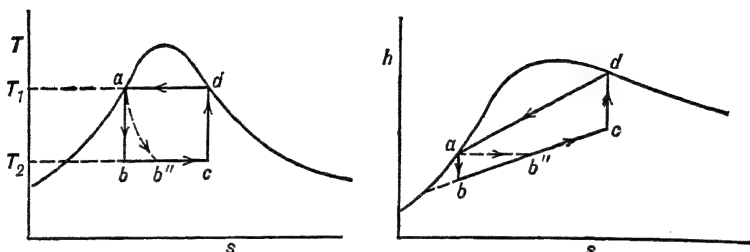


FIG. 118

with throttling $ab''cda$ is compared with the Carnot cycle $abca$ on a temperature-entropy diagram and on an enthalpy-entropy diagram. The process ab'' is shown as a line of constant enthalpy and represents

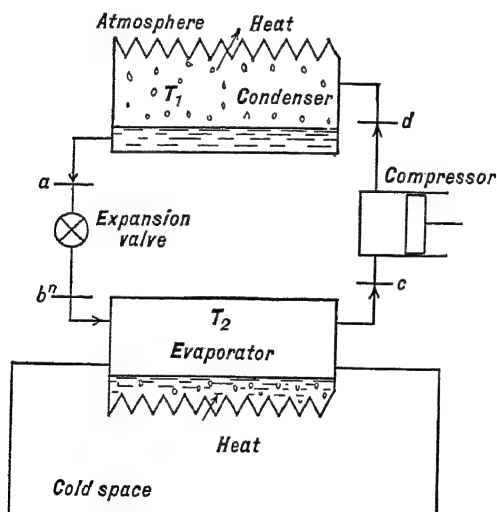


FIG. 119. The Compression Refrigerating Machine

the series of states that would be assumed by the fluid in flow through a porous plug of infinite fineness. (In flow through a throttle valve the series of states assumed is more nearly represented by the lines abb'' , the process bb'' being an irreversible decrease in velocity. Of course, when the fluid is in non-homogeneous states, such as those assumed while its velocity is decreasing irreversibly, no series of points on the diagram can represent the process.) Figure 119 is a diagram of a machine that employs the cycle $ab''cd$.

The compression process cd is executed in practice as nearly reversibly and adiabatically as possible. Most commonly a displacement (or reciprocating) type of compressor is used, though the turbine type

could be justified for very large machines. When large volumes of low-pressure vapor must be compressed, as in machines employing watervapor, an *ejector* is often used because the alternative is an extremely large and expensive compressor of either the reciprocating or the turbine type.

Coefficient of Performance

The *coefficient of performance* of a refrigerating machine is analogous to the efficiency of a heat engine. It is defined as *the ratio of the heat received by the machine from the body that is being cooled to the net work received*.

For a Carnot machine or any other reversible machine which receives heat reversibly at the lower temperature T_2 and rejects heat reversibly at the higher temperature T_1 the coefficient of performance may be found from the definition of the absolute scale of temperature. Thus, if q_1 is the heat rejected at temperature T_1 and q_2 is the heat received at temperature T_2 , the definition of the temperature scale requires that

$$\frac{q_1}{q_2} = \frac{T_1}{T_2}.$$

By the First Law, the net work of the cycle, W , is given by

$$W = q_1 - q_2,$$

so that the coefficient of performance, c.p., becomes

$$\text{c.p.} = \frac{q_2}{q_1 - q_2} = \frac{T_2}{T_1 - T_2}$$

Unlike the efficiency of a heat engine, the coefficient of performance may exceed unity, and in fact it approaches infinity as the temperature interval approaches zero.

By the usual reduction to absurdity method we shall prove that *no refrigerating machine can have a higher coefficient of performance than a reversible machine operating between the same levels of temperature*.

Assume a machine can be devised (*I*, Fig. 120) to work between temperatures T_1 and T_2 that has a higher coefficient of performance than a reversible machine operating between the same levels of temperature. Let a reversible machine (*R*, Fig. 120) operate between these levels, and let both machines *I* and *R* receive

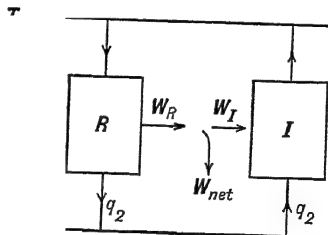


FIG. 120

from the lower level the same amount of heat q_2 . Since, by assumption,

$$\frac{q_2}{W_I} > \frac{q_2}{W_R},$$

where W_R and W_I denote respectively the quantities of work received by the reversible engine and the assumed engine, it follows that

$$W_R > W_I.$$

Now, if the reversible machine be reversed the heat source at lower temperature may be replaced by a conductor, and the reversible machine will supply sufficient work for the assumed machine and a surplus. Then the two machines in combination constitute a perpetual-motion machine of the second kind, which is impossible. Therefore, no machine can be devised to work between temperatures T_1 and T_2 that will have a higher coefficient of performance than a reversible machine.

Refrigerants

All the refrigerating machines discussed above absorb work, receive heat from a body at low temperature, and deliver heat to a reservoir at higher temperature, which is usually the atmosphere or a body of water. Such a machine is called a *compression* machine to distinguish it from other types which will be discussed subsequently.

The working fluid of a refrigerating machine is called the *refrigerant*. A large number of refrigerants are available to compression machines. Air has sometimes been used because it is free, abundant, and non-poisonous; but the coefficient of performance of air cycles is not favorable because constant-pressure processes are usually substituted for the impracticable isothermal processes of the Carnot cycle. An ideal vapor for use in a refrigerating machine would have among other characteristics a moderate vapor pressure at each limit of temperature in order that, first, the volume of the desired amount of fluid shall not be excessively large and so require large and expensive equipment, and, second, the stresses in the restraining walls shall be moderate.

Water, in view of these requirements, is barely acceptable over a narrow range of temperatures: say, between 35 F, where the density of the vapor is only 0.00034 lb/cu ft, and atmospheric temperature. In this range it may be used, at least in small installations, if some cheap substitute is found for the more expensive parts of the machine. Thus, we find water-vapor refrigerating machines (Fig. 121) being used for the limited range of refrigeration required for air conditioning. A

compressor for such a machine would be extremely large and expensive; therefore, an ejector is used, despite its low efficiency, to compress the vapor.

For refrigeration to temperatures below 32 F many vapors are available and new ones, usually organic compounds, are continually being discovered. The important properties of some of those commonly used or proposed as refrigerants are given in Table III and their vapor

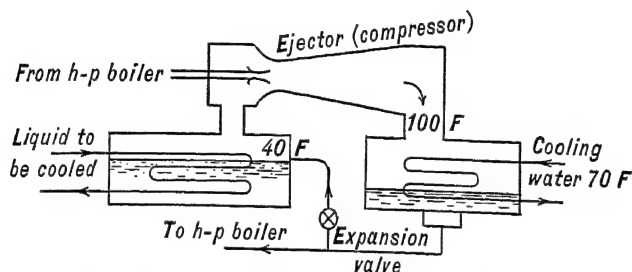


FIG. 121. Water-Vapor Refrigerating Machine

pressures are shown in Fig. 122. All would yield the same coefficient of performance between any two temperatures for a Carnot cycle; but irreversible expansion, or throttling, affects the coefficient to different degrees with different fluids. For example, the coefficient of performance of a Carnot cycle operating between 5 and 86 F is 5.74; for a cycle with irreversible expansion it is 4.85 for ammonia, 4.1 for water, and 2.56 for carbon dioxide. In this respect ammonia is superior to carbon dioxide as a refrigerant.

A practical refrigerant must yield a satisfactory coefficient of performance, have a freezing point below the lowest temperature in the cycle, have a moderate vapor density at the lowest temperature, be relatively stable chemically (that is, it must neither decompose nor react chemically with available metals), and, for household refrigeration in particular, be non-poisonous. Some of these requirements are met by a given fluid for one range of temperature but not for another. Thus we find that ammonia, though satisfactory for refrigeration to 0 F, will freeze at -108 F. Freon (CCl_2F_2), on the other hand, will not freeze above -247 F and therefore may be used to lower temperatures than ammonia.

TABLE III

PROPERTIES OF REFRIGERANTS

From *Refrigerating Data Book, A.S.R.E.*, 1939, p.

Name	Boiling Point F	Freezing Point F	Critical Point pressure temper- lb/in. ² ature F		Specific Heat of Liquid 5-86 F av.	Specific Gravity of Liquid $p = 1 \text{ atm}$
Ammonia, NH_3	- 28.0	-107.86	1651	271.2	1.12	.684
Butane, C_4H_{10}	33.1	-211.0	529.0	308.0	.54	.586
Carbon dioxide, CO_2	-109.3	- 69.9	1069.9	87.8	.77	1.56
Carbon tetrachloride, CCl_4	170.2	- 9.4	658.5	541.4	.20	
Dichlorodifluoro- methane, CCl_2F_2	- 21.7	-247	582.0	232.7	.23	1.48
Dichloroethylene, $\text{C}_2\text{H}_2\text{Cl}_2$	118.0	- 70.0	795	470.0	.268	
Dichloromonofluoro- methane CHCl_2F	48.0	-196.6	744	353.3	.24	1.348
Dimethyl ether, $(\text{CH}_3)_2\text{O}$	- 12.8	-216.0	765	260	.56	.72
Ethane, C_2H_6	-127.5	-278.0	718.0	89.8	1.1	.547
Ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$	61.6	-115.0	815	362	.63	
Ethyl bromide, $\text{C}_2\text{H}_5\text{Br}$	100.4	-182		447.0	.216	1.43
Ethyl chloride, $\text{C}_2\text{H}_5\text{Cl}$	54.4	-217.7	764.0	369.0	.428	
Ethylene, C_2H_4	-154.7	-272.0	749.0	49.5	1.35	.87
Ethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$	94.2	-177.34	521.0	382.0	.53	.72
Hexane, C_6H_{14}	155.9	-138.0	434.0	460.5	.60	.613
Isobutane, C_4H_{10}	14.9	-229.0	557.1	272.7	.62	.549
Methane, CH_4	-258.9	-297.0	672	-115.7		.308
Methyl chloride, CH_3Cl	- 10.6	-144	969.2	289.6	.38	1.002
Methylformate, $\text{C}_2\text{H}_4\text{O}_2$	89.3	-147.5	607.0	418.0	.51	.982
Methylamine, CH_3NH_2	20.3	-134.5	1082.0	314.0	.75	
Methylene chloride, CH_2Cl_2	103.7	-142.0	640.0	421.0	.33	1.291
Pentane, C_5H_{12}	97.1	-203	485	387.0		.610
Propane, C_3H_8	- 48	-309.8	632	204.1	.60	
Propylene, C_3H_6	- 52.5	-301.0	660	196.0		
Sulphur dioxide, SO_2	13.6	- 98.9	1141.5	314.8	.34	1.357
Trichloroethylene, C_2HCl_3	190.2	-124.3	728.0	520.0	.33	
Trichloromethane, CHCl_3	142.2	- 82.3	807.0	500.0	.23	1.47
Trichloromonofluoro- methane, CFCl_3	74.66	-168.0	636.0	388.4	.21	1.468
Trichlorotrifluoroethane $\text{C}_2\text{Cl}_3\text{F}_3$	117.9	- 31.0	499	417.4	.21	1.559
Water, H_2O	212.0	32.0	3206	705.4	1.0	

Absorption Machines

The ammonia absorption machine operates on the same cycle as the ordinary compression type of machine except that for compression of the vapor a group of three processes is substituted: first, absorption of the vapor into liquid water by the process of solution; second, compression of the solution to the higher pressure of the cycle; and third, generation of the vapor from the solution by heating. The simplest form of the machine is shown diagrammatically in Fig. 123, where the lines labeled T_0 , T_1 , and T_2 represent heat reservoirs that are respectively above the temperature of the atmosphere, at the temperature of the

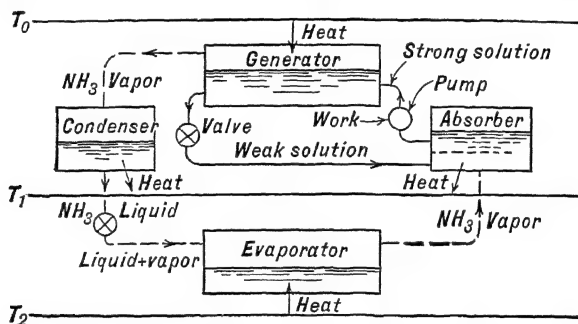


FIG. 123. Absorption Refrigerating Machine

atmosphere, and below the temperature of the atmosphere. Thus T_2 represents the body that is being refrigerated, T_1 the cooling water that is available, and T_0 a supply of steam.

It has been shown that the work of isentropic compression in steady flow is given by $\int_{p_1}^{p_2} V dp$,* where V denotes the volume of fluid to be compressed and p_1 and p_2 denote respectively the high and low pressures of the cycle. Now the volume of an ammonia solution which contains a certain amount of ammonia is a small fraction of the volume of that amount of ammonia when it is in a vapor state at the same pressure and temperature. Therefore, the work of compression of the solution is a small fraction of the work of compression of the vapor. In fact, if a solvent could be found that had an indefinitely high density, the work of compression would be vanishingly small.

However, where the work of compression is dispensed with, something equivalent to it must be provided to take its place. In the ammonia absorption machine it is a supply of heat at high temperature to the generator and a rejection of heat at atmospheric temperature from the

* See page 242.

absorber that takes the place of the work of compression. For it is well known that saturated ammonia vapor at atmospheric temperature will dissolve in water if the opportunity presents itself, and it is only by heating the solution well above atmospheric temperature that the ammonia vapor can be driven out of solution. Moreover, when ammonia dissolves in water the temperature of the liquid rises and the capacity of the solution for vapor thereby decreases; therefore it is only by cooling the solution that it can be made to absorb vapor again.

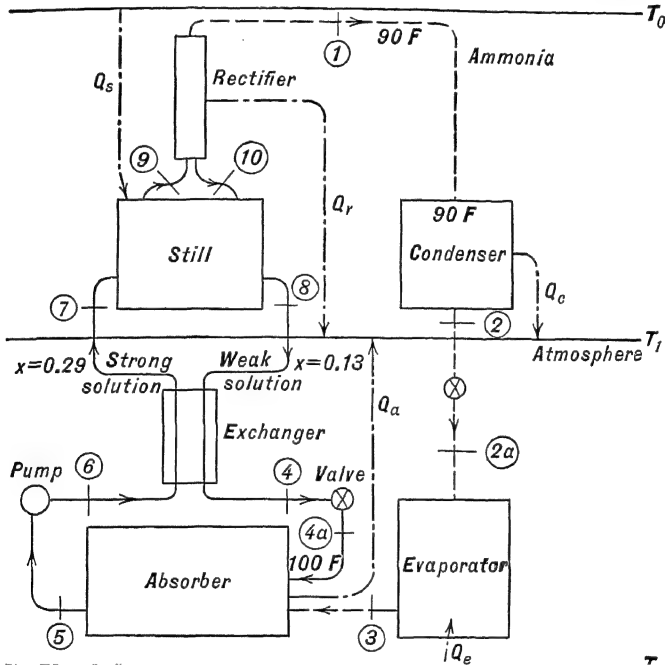


FIG. 124. Example of an Ammonia Absorption Cycle

EXAMPLE OF A FIRST-LAW ANALYSIS OF AN ABSORPTION CYCLE. In Fig. 124 is shown an ammonia absorption machine like that of Fig. 123 except that an exchanger and a rectifier are added. The exchanger heats the strong liquid going to the still as it cools the weak liquid returning from the still to the absorber. It exchanges no heat with any reservoir outside the fluid stream. The rectifier is a device which removes water from the vapor leaving the still, so that virtually pure ammonia vapor passes to the condenser. The purifying process is based on the fact that, when the mixture of vapors is cooled, more of the less volatile constituent — the water in this case — will condense out than of the other. Moreover the liquid condensed out of the purer vapor will be colder than the less pure vapor entering the rectifier and may

therefore be used to condense water out of the incoming vapor. Thus, in the rectifier, part of the vapor is condensed by rejecting heat Q_r to the cooling water or heat sink and the condensate is returned to the still, flowing counter to the vapor.

The following assumptions are made:

The strong solution leaving the absorber (5)* is 29 per cent NH_3 .

The weak solution leaving the still (8) is 13 per cent NH_3 .

The pressures in exchanger, still, rectifier, and condenser are identical and are equal to 180.6 lb/sq in. abs or 165.9 lb/sq in. gage.

The temperature in the evaporator is 10 F.

The vapor leaving the rectifier (1) is pure NH_3 and is at the saturation temperature corresponding to its pressure.

The vapor leaving the still (9) has the equilibrium concentration corresponding to the liquid leaving the still (8). This is equivalent to assuming such extreme turbulence within the still that the liquid inside is everywhere of the same composition as that coming out.

The condensate leaving the rectifier (10) is in equilibrium with the vapor entering it and is therefore of the same composition and in the same state as the solution leaving the still (8).

The liquid leaving the condenser (2) is saturated liquid at the pressure and temperature of the condenser.

The vapor leaving the evaporator (3) is saturated vapor at the temperature and pressure of the evaporator.

Solution enters the absorber (4a) at 100 F and leaves (5) at 80 F.

First, let us find the rate of flow of weak and strong solutions in terms of the rate of flow of pure ammonia to the condenser. Let w_n denote the mass of liquid or vapor that crosses the section labeled n in Fig. 124 for each unit mass of ammonia that crosses section 1, where n denotes any one of the labels corresponding to the sections of Fig. 124. Then we have for steady-flow conditions

$$w_1$$

and

$$w_7 = w_8 + 1, \quad [133]$$

because the amount of material stored in the still and rectifier does not change with time. For the flow of NH_3 , we may write

$$x_7 w_7 = x_8 w_8 + 1, \quad [134]$$

where x_n denotes the mass of NH_3 per unit mass of liquid or vapor at section n . Substituting the assumed values for x_7 and x_8 and solving [133] and [134], we get

$$w_7 = 5.44$$

and

$$w_8 = 4.44.$$

* The numbers in parenthesis refer to the sections correspondingly labeled in Fig. 124.

Next, let us find the amount of vapor leaving the still (9) and the amount of condensate returning to it (10). Equating flows into and out of the rectifier, we have

$$w_9 = w_{10} + 1. \quad [135]$$

For the ammonia alone, we have

$$x_9 w_9 = x_{10} w_{10} + 1. \quad [136]$$

By assumption, x_{10} is identical with x_8 , which is 0.13. The concentration x_9 , on the other hand, is that of vapor which is in equilibrium with a 13 per cent solution of ammonia at the pressure existing in the still. To find it we must employ tables of the properties of ammonia and of ammonia-water mixtures. For the former we shall choose the Bureau of Standards tables,* and for the latter the tables by Jennings and Shannon.† From the Bureau of Standards tables we find that the pressure of saturated ammonia vapor at 90 F is 180.6 lb/sq in. abs. This, then, is the pressure for sections 1, 2, 4, 6, 7, 8, 9, and 10. From the tables of Jennings and Shannon we find that vapor in equilibrium with a 13 per cent solution at a pressure of 180.6 lb/sq in. abs has a concentration, x_9 , of 0.602. Only w_9 and w_{10} remain unknown in [135] and [136], and these are found, upon solving the equations, to be

$$w_9 = 1.843$$

and

$$w_{10} = 0.843.$$

Now we may tabulate the properties of the streams of fluid crossing the various sections and their relative rates of flow. The values of the properties given in Table IV are found from the two tables cited above. It should be noted, however, that the tables of Jennings and Shannon give no values for liquid states other than saturated states. It would be accurate enough to assume that the enthalpy of a liquid is the same for a given temperature and concentration regardless of the pressure. Nevertheless, in the data given below the enthalpy was increased by 0.3 Btu/lb for each 100 lb/sq in. in excess of the pressure over the saturation pressure. Moreover, it was assumed that no change in temperature occurs across the pump.

Across any piece of apparatus the First Law may be stated in the form of the energy equation of steady flow, which simplifies to

$$Q = \sum (wh)_{\text{out}} - \sum (wh)_{\text{in}}, \quad [137]$$

where Q denotes the heat transferred in, $\sum (wh)_{\text{in}}$ the enthalpy of all the fluid that flows in, and $\sum (wh)_{\text{out}}$ that of all the fluid that flows out while unit mass of ammonia crosses section 1.

* *Tables of Thermodynamic Properties of Ammonia*, Circular of the Bureau of Standards, No. 142, 1923.

† *The Thermodynamics of Absorption Refrigeration*, The American Society of Refrigerating Engineers, 1938.

TABLE IV

Section	Phase l = liquid v = vapor	Pressure lb/sq in. abs	Temperature F	x	h † Btu/lb NH_3	w
1	v	180.6	90	1	554	1
2	l	180.6	90	1	65.6	1
2a	$v + l$	38.5	10	1	65.6	1
3	v	38.5	10	1	537	1
4	l	180.6	100	0.13	25.5	4.44
4a	l	38.5		0.13	25.5	4.44
5	l	38.5	80	0.29	-40.5	5.44
6	l	180.6	80	0.29	-40.1	5.44
7	l	180.6	236	0.29	134.1*	5.44
8	l	180.6	305.3	0.13	239	4.44
9	v	180.6	305.3	0.602	890	1.843
10	l	180.6	305.3	0.13	239	0.843

* From the energy equation of steady flow; see below.

† Values from the Bureau of Standards tables have been reduced by 77.9 Btu/lb to put them on the same base as those of Jeannings and Shannon.

For the heat exchanger as a whole the value of Q is zero; therefore, [137] becomes

$$0 = w_7 h_7 + w_4 h_4 - w_6 h_6 - w_8 h_8,$$

in which h_7 is the only unknown. Solving, we get

$$h_7 = 134.1 \text{ Btu/lb.}$$

For other pieces of apparatus only the value of Q is unknown, and the solution of [137] for each piece gives the following:

APPARATUS	Q
Condenser	-488.4 Btu/lb NH_3
Evaporator	471.4 " " "
Absorber	-870.5 " " "
Still	1770. " " "
Rectifier	-885. " " "

The Electrolux Refrigerator

The Electrolux refrigerator is a machine in which the required amount of work has been reduced to zero without the aid of a solvent of infinite density. Its design is based on the familiar fact that, when a volatile liquid is exposed to an inert atmosphere which contains little or no vapor of the liquid, the liquid will evaporate rapidly and its temperature will fall. For instance, physicians have long used a spray of liquid ether on local areas of the body to anesthetize those areas by freezing the tissues. In the Electrolux machine liquid ammonia is exposed to an atmosphere of hydrogen into which it evaporates while its temperature falls. This part of the cycle is analogous to the throttling operation

in the other cycles discussed above; in the throttling process the pressure of the fluid stream drops and evaporation occurs as the temperature falls, whereas in this process the liquid ammonia is exposed to a low *partial pressure* of its own vapor so that evaporation and cooling occur even though the pressure on the walls of the container is the same on either side of the point where the ammonia and hydrogen mix. The ammonia, being extremely soluble in water, is readily separated from the hydrogen by bringing the mixture in contact with water in an absorber. The solution passes to a generator in which the ammonia vapor is formed. The vapor, in turn, is condensed and returned to the evaporator where it mixes with the hydrogen coming from the absorber. The small pressure difference necessary to the circulation of the fluids is

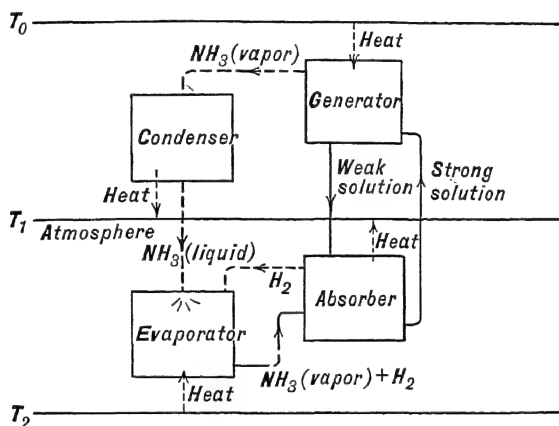


FIG. 125. The Electrolux Refrigerator

obtained by a heat pump or "percolator" in the generator. In Fig. 125 the arrangement of the parts of the machine relative to the three necessary temperature levels is shown diagrammatically.

The heat source at T_0 is a gas flame in the domestic refrigerator of this type. If the condenser and absorber are air-cooled then the refrigerator need be connected only to the supply of gas when it is installed. Its great advantage over the compression type of machine lies in the complete absence of moving parts, which makes for economy and dependability.

Silica-Gel Adsorption Machine

The attractive forces applied by a solid or liquid body on a surrounding gas or vapor cause a dense layer of gas or vapor of minute thickness to form immediately adjacent to the surface of the body. The material in this layer is said to be *adsorbed* on the surface of the body. If a solid

body is so finely divided that it has an extremely large amount of surface it can adsorb under some conditions relatively large amounts of vapor. At any one pressure of the vapor it will adsorb more at low temperatures than at high; and at any one temperature it will adsorb more at high pressures than at low. Thus, a solid which has adsorbed a vapor can be made to give off the vapor by heating; and a solid from which the vapor has been driven off can be made to adsorb vapor again by cooling.

A refrigerator has been devised which employs this principle. It comprises two masses of *silica gel*, an extremely porous, sandlike form of silicon dioxide. During the operation of the refrigerator one of these masses is cooled by air or water so that it will adsorb sulphur dioxide at a low pressure; the other, which has been previously charged with sulphur dioxide, is heated so that it will give off the vapor at a higher pressure. The vapor so generated passes to a condenser, and the liquid from the condenser expands through a throttle valve to the lower pressure maintained by the adsorbing mass. The cold liquid coming from the throttle provides refrigeration while it evaporates, and then its vapor passes to the cold silica gel where it is adsorbed. When the hot gel is free from adsorbed vapor and the cold gel is charged with vapor the functions of the two are exchanged by cooling the first and heating the second, while by suitable control of valves the generated vapor is caused to flow through the same path as before.

Zero-Work Machines and the Second Law

The performance of a zero-work machine, of which the Electrolux and the silica-gel machines are examples and which the ordinary ammonia-absorption machine approximates, is limited by the Second Law just as the performance of a compression machine is limited. To find this limitation let us consider a machine which receives no work and delivers none, but which takes in heat q_2 at a low temperature level T_2 and heat q_0 at a high temperature level T_0 , and rejects heat q_1 to an intermediate temperature level T_1 which for the machines in question represents the atmosphere. Now, such a machine might consist of a heat engine working between temperatures T_0 and T_1 and a refrigerating machine working between temperatures T_2 and T_1 , the refrigerating machine absorbing all the work produced by the heat engine. If both parts of the combination are reversible, then, by virtue of the definition of the absolute scale of temperatures, we may write for the work W_e of the reversible heat engine

$$W_e = q_0 \frac{T_0 - T_1}{T_0},$$

and for the work W_r of the refrigerating machine,

$$W_r = q_2 \frac{T_1 - T_2}{T_2}.$$

Since, by assumption, these two quantities of work are equal, we get for the ratio of the heat received from the cold body to the heat received from the hot body

$$\frac{q_0}{q_2} = \frac{T_0(T_1 - T_2)}{T_2(T_0 - T_1)}. \quad [138]$$

We shall prove next that of all possible machines that work between any three temperature levels, T_0 , T_1 , and T_2 , without flow of work to or from the environment, a reversible machine has the minimum value of the ratio of the heat received at the high temperature, q_0 , to the heat received at the low temperature, q_2 .

Assume that a machine can be devised (*I*, Fig. 126) of the type described that will have a lesser value of q_0/q_2 than a reversible machine (*R*, Fig. 126) using the same levels of temperature. Let the heat flow at level T_2 be the same for both machines, and let the reversible engine *R* be reversed. Then, by assumption, the heat q_0 delivered by engine *R* at temperature T_0 exceeds the heat q'_0 received by engine *I* at the same temperature. Since a conductor can be substituted for the reservoir at T_2 , the combination of machines *I* and *R* constitutes a self-acting device which causes heat to flow from level T_1 to level T_0 . With such means at our command we can readily devise a perpetual-motion machine of the second kind. But this is impossible. Therefore, no machine of this type can have a lesser value of q_0/q_2 than a reversible machine, and the right-hand member of [138] will always be less than the value of q_0/q_2 for any actual machine.

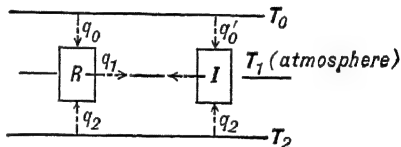


FIG. 126

Liquefying Air and Other Gases

It is entirely possible to liquefy air by means of any of the types of refrigerating machine described above provided that the liquids and vapors employed in the machine do not solidify at temperatures above the condensation temperature of air, namely, -312°F . Most of the fluids that meet this requirement have critical temperatures that are below the temperature of the available heat sink, so that rejection of heat cannot occur both at constant pressure and at constant temperature. But even if a refrigerant were found that was satisfactory in

these respects the apparatus necessary to economical production of liquid air would be complicated in design and awkward in operation.

Another possible method consists of using air as the working fluid in a compression type of refrigerating machine and expanding the air in a reversible adiabatic engine from a sufficiently high pressure so that it will partially condense. The liquid may be separated out and the remaining vapor recompressed to its original pressure. This cycle is shown on the temperature-entropy diagram of Fig. 127. The net work of this cycle would not be excessive if the work of expansion could be utilized in the compression process; but the consequent saving in power

would be too small to justify the cost of an efficient expansion engine except for very large projects.

Essentially isentropic expansion can be realized without the aid of an engine in the following manner: A chamber, with walls that are nonconducting to heat and low in heat capacity as compared with the fluid which fills the chamber, is charged with fluid at high pressure. The fluid

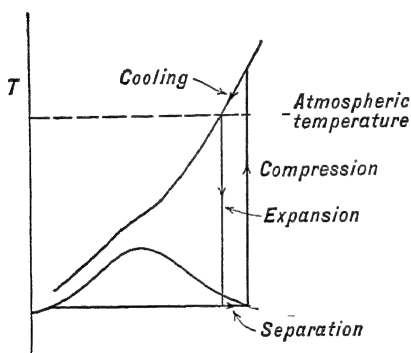


FIG. 127

is allowed to expand through a valve to the atmosphere or a low-pressure region. The fluid in the chamber does work on the gas passing into the valve just as it would do work on a piston moving in the same direction.

This process has been used in the liquefaction of gases, but it yields liquid only if transfer of heat from the chamber walls does not too gravely influence the state of the fluid. It is therefore particularly effective with fluids of high density. For example, it is a convenient way to solidify a liquid which would be dense enough to absorb the heat transferred from the walls of a well-designed chamber with little effect. In fact it is only necessary to use a good vacuum pump on liquid water in a Dewar flask to cause the water to freeze. In the same way liquid air or liquid hydrogen can be solidified by pumping vapor from a Dewar flask which contains the liquid.

The usual method of liquefying air, hydrogen, or any of the more permanent gases for laboratory or industrial purposes is the Linde regenerative process. The gas is first compressed and cooled to the temperature of the atmosphere or of some other available heat sink.

Now if the fluid were allowed to expand through a porous plug or an expansion engine the temperature of the fluid issuing from the expansion device would be somewhat lower than that of the fluid entering it; and if the issuing fluid were allowed to exchange heat with the entering fluid in counterflow the temperature of the fluid approaching the expansion point would be lowered. Therefore, a device similar to that shown in Fig. 128 can be used to cause a localized temperature depression in a stream of gas. (It should be noted that if a porous plug is used the Joule-Thomson coefficient for the gas must be greater than zero.) If the heat exchanger is made long enough, part of the gas may condense in the course of the expansion. That part may be drawn off as a liquid.

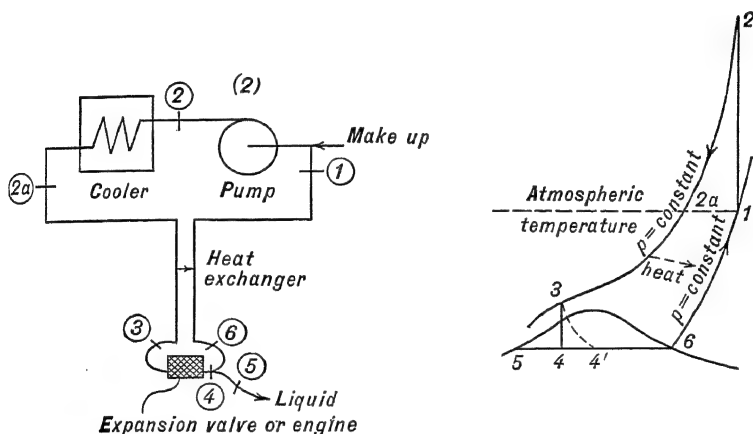


FIG. 128. The Linde Process for Liquefying Air

The idealized Linde process is shown on the temperature-entropy diagram of Fig. 128. Gas at atmospheric pressure and temperature, state 1, is compressed isentropically to state 2. In the cooler its temperature falls to that of the atmosphere (state 2a) at constant pressure. Next it enters the exchanger where it is cooled to state 3 by the gas issuing from the expansion device. It is expanded from state 3 to state 4 in a reversible adiabatic engine or from state 3 to state 4' in a porous plug. The liquid is separated in state 5, while the vapor in state 6 enters the exchanger and issues from it in state 1.

The following analysis gives the work required per unit of liquid produced in the idealized throttling process: Assume that resistance to the transfer of heat in the exchanger is so low that the temperature of the fluid leaving it in state 1 is only infinitesimally less than the temperature of the fluid entering it in state 2a. Let the mass of liquid produced per unit mass of fluid pumped be m , and let the pressure rise across the

pump, and the pressure fall in the expansion, be δp . Now we may write the energy equation of steady flow between section 2a on the one hand and sections 5 and 1 on the other. We get

$$h_{2a} = (1 - m)h_1 + mh_5,$$

where h denotes the enthalpy of unit mass of fluid, and the subscripts refer to the sections and states of Fig. 128. Solving the last equation for m , we get

$$m = \frac{h_1 - h_{2a}}{h_1 - h_5},$$

which for small values of δp may be written

$$m = \frac{-c_1 \delta p}{h_1 - h_5},$$

where c_1 denotes $(\partial h / \partial p)_t$, the constant-temperature coefficient at state 1. The work required to compress each unit mass of fluid entering the pump for small values of δp is given by

$$W = v_1 \delta p,$$

where v_1 denotes the specific volume of the fluid at section 1. The work of compression per unit mass of liquid produced is, therefore,

$$\frac{W}{m} = -v_1 \frac{h_1 - h_5}{c_1}. \quad [139]$$

For liquefying air at 70 F the work per pound of liquid is 4.9×10^7 ft-lb by [139].*

This same analysis may be applied to large values of δp to show that the work per unit mass of liquid decreases with increase in the range of compression and expansion until the pressure is approached at which the coefficient c changes sign.

In the liquefaction of helium, which occurs at 4.3 K, it is usual to use liquid hydrogen at 20 K as the heat sink. In the liquefaction of hydrogen, liquid air may be used as the heat sink, but it leaves an unusually large range of temperature, 20 to 82 K, for the refrigerating process to span. It is therefore sometimes advantageous to cool the hydrogen first in a preliminary process in which the adsorbed phase of hydrogen on charcoal at temperatures above the critical temperature is used in place of the liquid phase of air. By expanding the gas which surrounds the charcoal the temperature of the system is decreased. It is now

* Approximate values for the quantities in [139] are as follows: $v_1 = 13.35$ ft³/lb, $(h_1 - h_5) = 177$ Btu/lb, $c_1 = -0.1020$ Btu/lb atm.

possible to transfer a relatively large amount of heat from the hydrogen to be cooled, to the expanded hydrogen and its adsorbed phase, as the latter evaporates off the surface, without much rise in the temperature of the charcoal and its hydrogen. The charcoal may be charged again at the sink temperature when gas is returned to it under pressure.

Fractional Temperatures on the Kelvin Scale

The expansion of helium to atmospheric pressure may reduce the temperature to the normal boiling point of helium, 4.3 K. A temperature of about 0.8 K* has been achieved by expansion to 1/6000 of an atmosphere. Further refrigeration by this method is impracticable for ordinary laboratory operations; and since helium has the highest known vapor pressure at these temperatures we may conclude that refrigeration by expansion of liquids and vapors cannot be extended appreciably below 1 K. Nevertheless, it is desirable to have means of refrigerating to even lower temperatures for scientific purposes. Fortunately, most substances, metallic and non-metallic, become magnetic to some degree at these very low temperatures, and refrigeration can be accomplished by a cycle of magnetization, for it is well known that most magnetic substances rise in temperature when magnetized and fall in temperature when demagnetized. In order to refrigerate a magnetic solid, therefore, it is only necessary to cool it to the temperature of the sink (say, liquid helium) after magnetizing it in a strong magnetic field, and then to reduce the magnetic field. For this purpose magnets have been devised that will produce extremely high magnetic fields, and with their aid temperatures of the order of 0.01 K have been attained. *

PROBLEMS

1. A "warming engine" which is to be used to heat a house consists of a cycle of processes each of which is carried out in steady flow. The working fluid is H_2O . It receives heat in an evaporator at 35 F from the outdoor atmosphere. Saturated vapor at 35 F is compressed reversibly and adiabatically to 2 lb/sq in. abs. Upon leaving the compressor it is introduced into radiators in the house, where it gives up heat until it is reduced to saturated liquid at 1 lb/sq in. abs. Finally it expands through a throttle valve into the evaporator.

(a) Find the amount of heat supplied to the house per kilowatt-hour of work supplied to the warming engine.

(b) Compare the cost of heating the house by means of the warming engine with the cost of fuel for direct heating from the combustion of coal. Assume that 1 kw-hr

*From existing evidence it appears that helium has no vapor-liquid-solid triple point, and that it can be solidified only by means of pressures well in excess of 1 atmosphere. Therefore, the liquid cannot be solidified at atmospheric pressure by pumping off vapor.

of electrical work costs 4 cents, 1 ton of coal costs \$10, and that 14,000 Btu of heat can be obtained for each pound of coal consumed.

2. In a refrigeration cycle, saturated water vapor at 40 F is compressed reversibly and adiabatically to the pressure corresponding to saturated vapor at 80 F. Find the temperature, enthalpy, and specific volume of the vapor at the end of compression. It may be assumed that the specific heat of superheated water vapor at constant pressure is constant and equal to 0.45 Btu/lb F.

3. Consider a refrigeration cycle with H_2O as the refrigerant that will receive heat at 40 F and reject heat at 80 F (minimum). Saturated vapor is withdrawn from the evaporator and is compressed in a reversible adiabatic compressor. Saturated liquid is withdrawn from the condenser and is expanded through a throttle valve.

(a) Describe the state of the fluid where it issues from the compressor and that where it issues from the throttle valve.

(b) Find the amount of heat received by each pound of H_2O at 40 F.

(c) Find the coefficient of performance.

Find the coefficient of performance of this cycle after it has been modified by:

(d) substituting a reversible adiabatic engine for the throttle valve;

(e) compressing reversibly and adiabatically to a saturated state instead of from a saturated state;

(f) making the substitutions prescribed in (d) and (e) simultaneously.

(g) Find the coefficient of performance of a Carnot refrigerating cycle which operates between the same temperature limits.

4. In the preceding problem, substitute NH_3 for H_2O and answer questions (a) to (g). For the cycle without modification compare the volume of saturated ammonia vapor received by the compressor per Btu of heat received at 40 F with the corresponding volume of water vapor.

5. A compression type of refrigerating machine which employs ammonia as the refrigerant delivers saturated vapor at the temperature in the evaporator to a reversible adiabatic compressor. Liquid leaving the condenser is expanded through a throttle valve to the pressure in the evaporator. The temperature in the condenser depends upon the temperature of the available cooling water. For an evaporator temperature of 5 F plot the coefficient of performance against temperature in the condenser for temperatures ranging from 40 F to 120 F.

For a condenser temperature of 60 F plot the coefficient of performance against temperature in the evaporator for temperatures ranging from -40 F to 32 F.

For a condenser temperature of 60 F plot the coefficient of performance if the work of compression is 25 per cent in excess of the reversible work (the compression process being adiabatic, though not reversible).

6. An air cycle consists of reception of heat at constant pressure, isentropic compression, rejection of heat at constant pressure, and isentropic expansion. The temperature of the body that is being cooled is constant at 0 F, and heat is to be rejected to cooling water at 60 F. If the pressure of the air is 1 atmosphere where it receives heat, what is the minimum permissible pressure where it issues from the compressor?

7. Assume that the absorption cycle given in the example on page 251 is modified by increasing by 50 per cent the flow of ammonia solution through the pump. The

maximum temperature in the still is to remain unaltered; that is, state 8 is unaltered. The assumptions regarding the states 1, 2, 3, and 4a and the temperatures in the condenser, in the evaporator, and at 5 are to remain unaltered. Prepare a table for this problem similar to that given in the example, and calculate the various heat quantities.

8. If the temperature T_0 in the absorption cycle shown in Fig. 124 is to be decreased by 30 F without alteration in the temperature in the condenser, what alterations would be necessary in the values assumed for that cycle?

9. Using the data given in the footnote on page 260 verify the figure given on that page for the work per pound of liquid air.

10. Analyze the problem of determining the work per pound of liquid air produced for finite values of δp . (Ignore the difference in composition of the vapor at 6 as compared with the vapor at 3.) Assuming c to be constant and equal to -0.102 Btu/lb atm, calculate and plot the work per pound of liquid air against δp .

SYMBOLS

c	constant-temperature coefficient $(\partial h / \partial p)_t$
c.p.	coefficient of performance
h	enthalpy per unit mass
m	mass
p	pressure
q	a positive number representing a quantity of heat
Q	heat to system
s	entropy per unit mass
T	absolute temperature
u	internal energy of unit system in the absence of motion, gravity, etc.
V	volume
w	mass rate of flow
W	net work of cycle

SUBSCRIPT

t	constant temperature
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CHAPTER XVI

HEAT AND POWER FROM COMBUSTION

Most of the means by which work is produced for industrial and domestic purposes are based on a process called combustion, which is a chemical reaction between oxygen in the air and a fuel. In a steam power plant the fuel is usually coal or heavy oil; in an internal-combustion plant it is commonly light oil. There is an essential difference between the steam power plant and the internal-combustion plant in that the former includes within it a device which is a heat engine in the thermodynamic sense and the latter does not. The working fluid in the heat engine of the steam power plant passes through a cycle.* The efficiency of this cycle in the production of work is comparable to (but cannot exceed) that of a Carnot cycle. The working fluid of the internal-combustion plant, on the other hand, never returns to its initial state; therefore, its performance cannot be directly compared with that of a Carnot engine.

Combustion as a Source of Heat

Inside the ordinary central-station steam power plant is a heat engine comprising a stream of water which passes through a cycle of changes of state and delivers work. The air and fuel which enter such a plant and leave as products of combustion serve merely as a source of heat for the heat engine. Let us determine the maximum quantity of heat that can be made to flow from this source to the heat engine.

The air-fuel stream enters the plant practically at the pressure and temperature of the atmosphere and leaves it at the pressure of the atmosphere. During its progress through the plant it is cooled by contact with parts of the heat engine. The lowest temperature of any part of the heat engine is the temperature of the atmosphere — or, what is approximately the same, the temperature of the water available for cooling. In the limiting case, therefore, the air-fuel stream would be cooled to the temperature of the atmosphere before being rejected.

* The steam power plant is considered here to operate condensing. The water employed by a locomotive, for example, does not pass through a cycle of operations, though for purposes of comparison it is sometimes assumed that the cycle is closed by an imaginary condensation process.

The process experienced by the air-fuel stream when it serves as a source of heat is a steady-flow process in which no work crosses the boundaries of the stream, however much flow work may be done at the entrance and exit of the apparatus. It is shown diagrammatically in Fig. 129. For such a process the heat transferred *outward* is given by

$$-Q = H_0 - H_1,$$

where H_0 denotes the enthalpy of a given mass of the compound stream entering and H_1 the enthalpy of the same mass of the single stream leaving. In order that $-Q$ should be at a maximum value the temperature must be the same at 1 as at 0, as explained in the preceding paragraph. It is also necessary, however, that the enthalpy at 1 be the minimum possible enthalpy corresponding to the pressure and temperature of the atmosphere — the pressure and temperature that prevail, by assumption, at 0. For the combustion

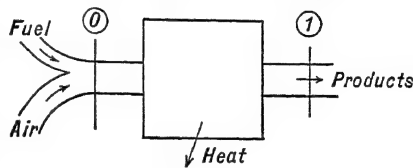


FIG. 129

of coal or of any of the common types of hydrocarbon fuels the condition of minimum enthalpy corresponds closely to the condition of complete combustion:* the condition for which carbon appears only in the combined form CO_2 and hydrogen only in the combined form H_2O . The maximum possible transfer of heat can, therefore, be determined by means of an apparatus such as that shown in Fig. 129 from which the products would leave in the completely burned state.

The excess of the enthalpy of a given mass of fuel and air over the minimum possible enthalpy of that mass at the same pressure and temperature may be used as a rational criterion by which the quality of performance of any steam generator or steam power plant may be judged. A rational efficiency η_θ of a steam generator is, therefore, given by

$$\eta_\theta = \frac{q}{H_0 - H_{\min}}$$

where q denotes the heat transferred to the H_2O system in the time required for unit mass of fuel in the air-fuel stream to enter the apparatus, and H_0 and H_{\min} , denote respectively the enthalpy at entrance and the minimum possible enthalpy of the air-fuel stream per unit mass

* It also corresponds closely to the condition of minimum Z , which is the condition of greatest stability. If this were not so, then it would be possible to carry out an *endothermic* change from the condition of minimum enthalpy to the condition of stability. Such a change could be used for refrigeration or for the production of work.

of fuel. Similarly, a rational efficiency η_p of the power plant is given by

$$\eta_p = \frac{W}{H_0 - H_{\min.}}$$

where W denotes the work produced by the power plant in the time required for unit mass of fuel in the air-fuel stream to enter the apparatus.

It is true that the value of this criterion changes with the ratio of fuel to air in the stream, but the change is of little consequence unless the amount of air supplied is inadequate for complete combustion. This condition is seldom encountered in combustion for heating purposes.

When solid fuels are employed the measurement of $(H_0 - H_{\min.})$ by means of a steady-flow process becomes difficult. Since no convenient alternative means has been devised, another criterion is used which is more readily measured, though less readily justified. This criterion is the *bomb-calorimeter heating value*. It is obtained by measuring the heat transferred from a mixture of fuel and oxygen when the system changes to a stable state (which is one of essentially complete combustion) at the initial temperature and volume.

The bomb calorimeter measures a change in internal energy; the flow calorimeter, on the other hand, measures a change in enthalpy. If the final states of the two processes were identical this distinction would make little difference in the measured values per unit mass of fuel. The final states differ primarily in that the concentration of water in the products of combustion is much higher in the bomb calorimeter than in the flow calorimeter because of the presence of nitrogen in the latter. If the fuel contains much hydrogen, liquid water may form in the bomb calorimeter and not in the other. For this reason the bomb-calorimeter heating value is the larger of the two and is sometimes called the *higher heating value*. The difference between the two heating values is often large enough to be important.

Thus, the quantity called a heating value is determined in an arbitrary type of process which involves a unit mass of fuel. The efficiency of a power plant which includes a heat engine is often defined as the quotient obtained when the work produced is divided by the heating value corresponding to one of these arbitrary processes; thus,

$$\eta_p = \frac{W}{\overline{HV}},$$

where η_p denotes the efficiency, W the work produced, and \overline{HV} the heat-

ing value, the last two being expressed in the same units.* The only justification of this procedure is that the heating value is an approximation to the maximum possible decrease in the enthalpy of unit mass of fuel in combination with the air that accompanies it as it enters the power plant.

Combustion as a Source of Power

It was pointed out at the beginning of this chapter that the steam power plant is unlike the internal-combustion power plant in that the former includes a system which operates in cycles — a heat engine — and the latter does not. Nevertheless, from an external viewpoint the two are quite similar. Thus, the diagram of Fig. 130, which shows a power plant continuously receiving air and fuel, and continuously delivering work, products of combustion, and heat to the surroundings, serves to represent either type. The heat rejection may be of different orders of magnitude in the two cases, because the steam plant

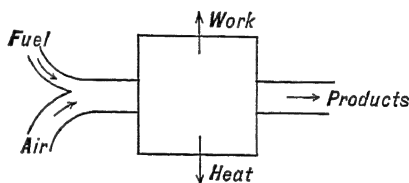


FIG. 130

rejects heat in order to condense the working fluid, whereas the internal-combustion plant rejects heat to prevent the loss in rigidity and strength of its metal parts through excessive rise in temperature.

In order to arrive at a rational criterion by which any power plant represented by Fig. 130 can be judged, let us derive an expression for the maximum possible work that can be obtained by any means from the stream of air and fuel between the time it enters the plant and the time it leaves as products of combustion:

First, it can readily be seen that the maximum work will not be obtained from a given stream of air and fuel unless its constituent matter, in whatever form, leaves the plant at the temperature and pressure at which it enters, namely, the temperature and pressure of the environment. For if the pressure were different it would be necessary to discard the fluid in a series of tight containers, and work could be obtained from each container by allowing one of its walls to move until equilibrium of pressure was established. (The fluid could be discarded as a free stream only at atmospheric pressure.) If the temperature were different it would be possible to operate a heat engine between the temperature of the fluid and the temperature of the environment and produce work.

* There is a similar expression for the efficiency of a steam generator:

$$\eta_o = \frac{\dot{A}}{H\dot{V}}.$$

Second, it was shown on page 236 that, by virtue of the statement

$$dS \geq \frac{dQ}{T}, \quad [16]$$

the maximum amount of useful work that can be obtained from any system when it passes from one state at a given pressure and temperature to another at the same pressure and temperature is the decrease between those two states in the value of Z . This maximum can be realized only in a reversible process joining the two states.

Third, the maximum useful work that can be delivered by a unit mass of the air-fuel stream will, therefore, be the maximum possible decrease in its value of Z at the pressure and temperature of the environment. We may, then, express the maximum useful work as

$$W_u = Z_0 - Z_{\min}. \quad [140]$$

where Z_0 denotes the value of Z , $(H - TS)$, for the given mass of the air-fuel stream at the pressure and temperature of the environment, and Z_{\min} the minimum value of Z for that same collection of matter at the same pressure and temperature.

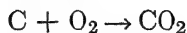
It is shown on page 415 that a system is in its most stable state at a given pressure and temperature when the value of Z is a minimum. Therefore, the maximum work can be obtained only if the air-fuel system is allowed to proceed to its most stable state. This conclusion is in accord with the common observation that any departure of a system from stable equilibrium with its environment represents an opportunity to produce work.

The most stable state of a system consisting of a mixture of air and fuel at the pressure and temperature of the atmosphere is one in which virtually all the carbon in the fuel is in the combined form CO_2 and virtually all the hydrogen in the fuel is in the combined form H_2O , provided only that enough oxygen was present in the system originally to permit the change. For such a state of the system it is possible with existing data to compute the corresponding value of Z , which when subtracted from the value of Z corresponding to the original state yields the maximum useful work.

For example, a mixture of pure carbon (graphite) and oxygen in the proportions one mole of carbon to one mole of oxygen at a pressure of 1 atmosphere and at a temperature of 77 F has a value of Z which is higher than that of carbon dioxide at the same pressure and temperature by 14,140 Btu per pound of carbon in the mixture.* It would be possible,

* Within the experimental error in this figure, the maximum heat of combustion in steady flow $(H - H_{\min.})$ is identical with it.

therefore, to obtain from the reaction



14,140 Btu of work per pound of carbon burned. A good steam power plant obtains less than one-third of this amount for each pound of carbon burned.

Let us consider how this maximum work can be realized. The statement [16], as is shown on page 236, reduces to

$$W_u \leq Z_0 - Z_f, \quad [141]$$

where W_u denotes the useful work, or work in excess of that necessary to displace the environment, and subscripts 0 and f refer to initial and final states respectively. The maximum useful work is obtained, then, if the sign of equality holds in this statement and in [16] as well, that is, if the process is reversible.

In order to change a mixture of reactants (such as C and O_2) to products (such as CO_2) reversibly, we might first bring the mixture reversibly to a state in which the reactants could coexist in stable equilibrium with an infinitesimal amount of the products — that is, a state in which the tendency toward chemical reaction has vanished. Then the mixture could be gradually and reversibly altered in pressure and temperature, by means of motion of a piston and of reversible exchange of heat with the atmosphere, while it follows a path of most stable states of progressively greater degrees of combination. The reaction would be virtually complete at atmospheric pressure and temperature, and the net work of the entire process would be $(Z_0 - Z_f)$.

If it is difficult to attain a stable state of complete dissociation (as it is for C and O_2) it might be necessary to find a chain of reactions involving other substances. For example, the fuel might be combined with some third material with which it will react reversibly. If the products of this reaction will unite reversibly with air to restore the third material to its initial state and leave only the usual products of combustion, then the products could be formed reversibly from fuel and air. For reversible execution of this chain of reactions by means of motion of a piston and reversible exchange of heat with the atmosphere, the work delivered would be $(Z_0 - Z_f)$.

In order that the exchange of heat with the atmosphere at temperature T_0 should be reversible in these processes, the system at the time of the exchange must be at the temperature T_0 , or there must be interposed between the system and the environment a reversible heat engine. A rise in temperature of the system may, therefore, be caused by heat which is pumped by the heat engine from the atmosphere, or by reversi-

ble adiabatic compression of the system through motion of the piston, or by both heat and compression. Similarly, a fall in temperature may be caused by transfer of heat to a heat engine, or by reversible adiabatic expansion, or by both. Regardless of the details of the process, the net useful work delivered will be $(Z_0 - Z_f)$.

The reactants in a process may be changed reversibly to the products of the reaction by another method which does not involve high temperatures. In this method, which may be illustrated by the ordinary lead storage cell, the reactants are first brought into equilibrium by applying a difference in electrical potential between them which annuls the tendency toward chemical reaction. If the difference in potential is reduced slightly by allowing a small electric current to flow from the side of high potential through a reversible motor to the side of low potential, the reactants will combine until a new equilibrium is established corresponding to the new value of the difference in potential. During this process the electric motor can be made to raise a weight. The process is evidently reversible, because an infinitesimal increase in the magnitude of the weight would cause the weight to fall, the current to flow in the reverse direction, and the products of the reaction to dissociate.

If the reactants were brought into equilibrium in a cell and a minute electric current were withdrawn, the reaction would proceed reversibly while heat would be exchanged reversibly with the environment. The electrical work delivered outside the system would then be equal to the maximum possible work, which is in turn equal to the decrease in the value of Z , or $(Z_0 - Z_f)$. Such processes have been realized, essentially, for many chemical reactions, but a practicable electric cell for combining carbon and oxygen has not yet been devised. When it is devised the work obtained from a pound of coal will be from two to three times as great as at present.

The Internal-Combustion Engine

The internal-combustion engine is a special case of the combustion power plant. Since, in a thermodynamic sense, no transfer of heat is necessary to its operation, the large heat-transfer surfaces employed by heat engines are dispensed with. Therefore, it is a compact power plant.

When a fluid is raised in temperature by means of a transfer of heat the highest temperature attained by it must always be less than the highest temperature that the restraining walls can sustain, because transfer of heat requires that the walls should be hotter than the fluid.

If the fluid is raised in temperature by other means (such as compression or combustion) its temperature may exceed this limit, because the walls may be kept cooler than the fluid. Thus the fluid in the internal-combustion engine may attain higher temperatures than the fluid in a heat engine, and these higher temperatures result in high efficiency in the production of work.

The Otto Engine

The commonest type of internal-combustion engine is known as the Otto engine. It is the type used in virtually all automobiles and airplanes. The processes through which the air-fuel mixture passes in an Otto engine are illustrated in Fig. 131 and may be described as follows:

ab. A mixture of air and fuel is drawn into the cylinder through an open valve as the piston moves outward.

bc. The mixture is compressed, all valves being closed, as the piston moves inward.

cd. The mixture is ignited by means of an electric spark when the piston is near the inward end of its stroke; combustion occurs and the mixture of air and fuel becomes a mixture of products of combustion at a higher pressure and a higher temperature.

de. The products of combustion are expanded as the piston moves outward.

ef. They expand into the exhaust passage when the exhaust valve opens near the outward end of the stroke.

fa. The fluid remaining in the cylinder is pushed through the exhaust valve as the piston moves inward.

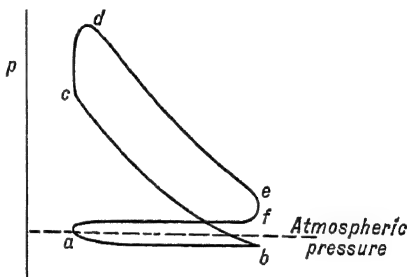
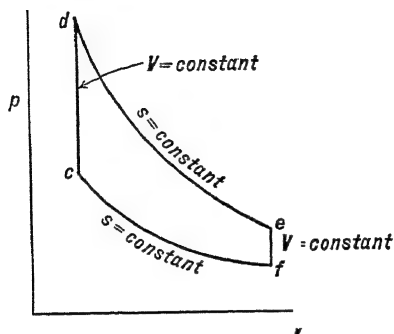


FIG. 131. Indicator Diagram of an Otto Engine

The analysis of these processes is sufficiently involved to encourage the application of simplifying assumptions of varying degrees of reality. The first simplification that we shall consider, the *air-standard cycle*, consists of the substitution for the internal-combustion engine of a heat engine with an indicator diagram that resembles that of the actual engine.

The Air-Standard Cycle

Consider a heat engine consisting of a mass of air confined in a cylinder by a piston. Let the air pass through the cycle of operations illustrated in Fig. 132, which may be described as follows:



fc. The air is compressed reversibly and adiabatically.

cd. It is heated at constant volume.

de. It is expanded reversibly and adiabatically.

ef. It is cooled at constant volume to its original state.

FIG. 132. The Air-Standard Otto Cycle

The indicator diagram *fcdef* of Fig. 132 differs from that of Fig. 131 only in that the negative loop of suction and discharge *fab* has vanished and the rounded corners of the remainder of the diagram have been sharpened. The first of these differences would not exist if in the actual engine there were no throttling in the ports, and the second would not exist if in the actual engine combustion and equalization of the pressures on two sides of a valve could be accomplished instantaneously.

Let us determine the efficiency of the air-standard Otto cycle. If we assume air to be a perfect gas, then the heat q_1 added from the source per pound of air is given by

$$q_1 = c_v(T_d - T_c),$$

where c_v denotes the specific heat at constant volume for air, and T the absolute temperature of the state indicated by the subscript and the corresponding letter in Fig. 132. Similarly, the heat q_2 rejected to the sink is given by

$$q_2 = c_v(T_e - T_f).$$

The efficiency is then

$$\eta = \frac{q_1 - q_2}{q_1}$$

$$1 - \frac{T_e - T_f}{T_d - T_c}$$

The reversible adiabatic processes *de* and *fc* can be represented by the relation

$$pv^k = \text{constant},$$

where k is a constant and equal to 1.4. Therefore

$$\frac{T_c}{T_f} = r^{k-1} = \frac{T_d}{T_e},$$

where r denotes the compression ratio v_f/v_c or the expansion ratio v_e/v_d . It follows that

$$= 1 - \left(\frac{1}{r}\right)^{k-1}. \quad [142]$$

The variation of the efficiency of an air-standard Otto cycle with compression ratio as given by [142] is shown by the upper curve in Fig. 133. Comparison of this curve with the corresponding curve for an internal-combustion Otto engine, which is also shown, indicates that the air-standard analysis gives efficiencies well in excess of those of the actual engine, though in other characteristics the curves resemble each other.

The Diesel Engine

If the compression ratio (v_f/v_c , Fig. 132) is too great in an internal-combustion engine the fuel may ignite as a result of the rise in temperature that accompanies compression. In order to delay ignition it may be necessary to withhold introduction of the fuel until the stroke is nearly completed. Then the rate at which fuel is introduced will govern the rise in pressure that accompanies combustion, and it may even be made to eliminate that rise if the pressure at the end of compression is the maximum desirable pressure. In that event the indicator diagram would

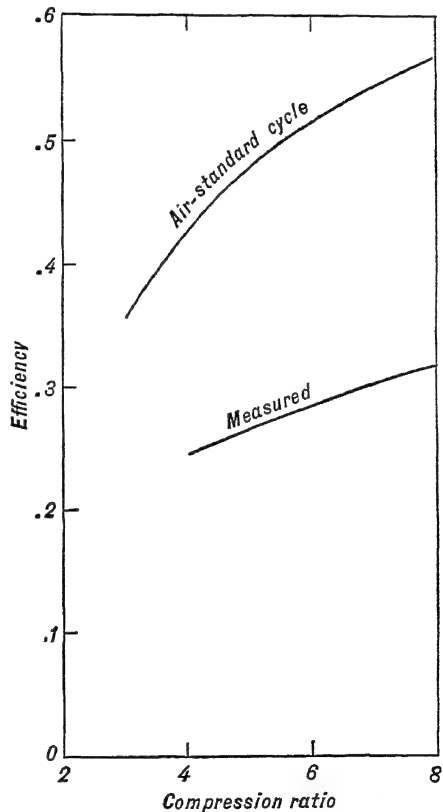


FIG. 133. Comparison of the Air-Standard Cycle and the Otto Engine Process

The measured values were obtained in the Sloan Laboratory of M. I. T. and are presented through the courtesy of Professor C. F. Taylor.

be as shown in Fig. 134 and the engine would be called a Diesel engine.

The corresponding air-standard cycle is shown in Fig. 135. The efficiency of this cycle cannot be expressed in terms of compression ratio, V_1/V_2 , alone, because the expansion ratio, V_4/V_3 , can be altered indepen-

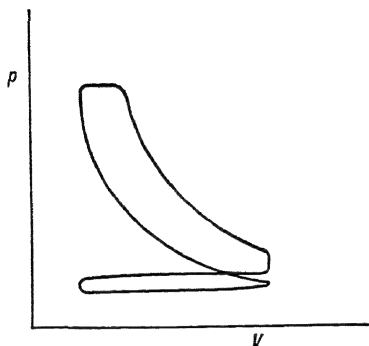


FIG. 134. Indicator Diagram of a Diesel Engine

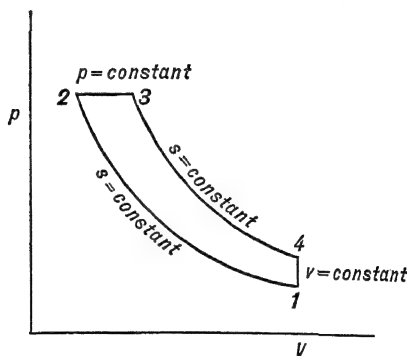


FIG. 135. The Air-Standard Diesel Cycle

dently of the compression ratio. Letting r_c denote the compression ratio and r_e the expansion ratio, we get for the efficiency of the air-standard Diesel cycle

$$\eta = 1 - \frac{1}{k} \left[\frac{(1/r_e)^k - (1/r_c)^k}{(1/r_e) - (1/r_c)} \right]. \quad [143]$$

An equivalent expression in terms of the ratio of expansion during heating (or combustion), $r_b = V_3/V_2$, is

$$\eta = 1 - \frac{1}{r_c^{k-1}} \left[\frac{r_b^k - 1}{k(r_b - 1)} \right]. \quad [144]$$

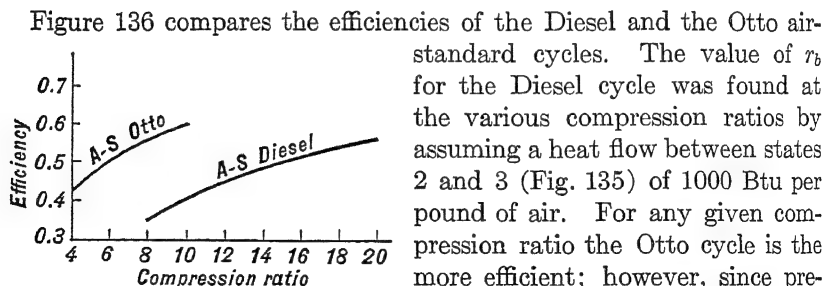


FIG. 136. Comparison of Efficiencies of Air-Standard Cycles

From Taylor and Taylor, *The Internal-Combustion Engine*, International (1938), p. 12.

Figure 136 compares the efficiencies of the Diesel and the Otto air-standard cycles. The value of r_b for the Diesel cycle was found at the various compression ratios by assuming a heat flow between states 2 and 3 (Fig. 135) of 1000 Btu per pound of air. For any given compression ratio the Otto cycle is the more efficient; however, since pre-ignition limits the compression ratio of the Otto engine but not that of the Diesel engine, the Diesel

engine is commonly operated at such high compression ratios that its efficiency is greater.

The actual Diesel engine has another important advantage over the Otto engine; namely, it can operate with lower ratios of fuel to air. This, in combination with high compression ratio, accounts for its high efficiency.

Analysis of Simplified Otto-Engine Processes

The air-standard cycle can yield only a limited amount of information about the non-cyclic internal-combustion-engine process. A study of the internal-combustion-engine process itself requires more elaborate data, but it can be justified by the closer approximation of its results to the performance of the engine.

Let us consider the simplified Otto-engine processes illustrated in Fig. 137. Process 1-2 is a reversible adiabatic compression of the charge of fuel and air mixed with a small amount of products from previous operations. Process 2-3 is a constant-volume change of state resulting from combustion. Process 3-4 is a reversible adiabatic expansion of the products of combustion. Process 4-5 is a change of state corresponding to release of some of the mixture of products from the cylinder while the piston remains stationary. Process 5-6 is an expulsion of most of the remaining gas from the cylinder at constant pressure. Process 6-1 is a mixing at constant pressure of fresh charge of fuel and air with the gases remaining from the previous stroke.

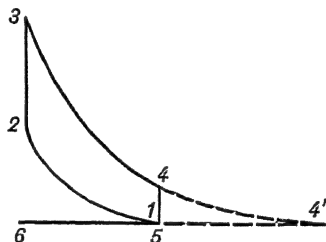


FIG. 137

For each of these processes we may write [2a] in the form

$$Q = \Delta E + W.$$

Ignoring exchange of heat with the cylinder walls, we get for the first three processes the following:

1-2. A process at constant entropy.

$$W_{12} = E_1 - E_2.$$

2-3. A process at constant volume.

$$E_3 = E_2.$$

3-4. A process at constant entropy.

$$W_{34} = E_3 - E_4.$$

The net work W_n of the entire series of processes 1-2-3-4-5-6-1 is, therefore,

$$W_n = E_1 - E_2 + E_3 - E_4,$$

which is also equal to the area enclosed by the indicator diagram and to the change in enthalpy of the charge admitted in process 6-1 between its state in the inlet duct and its state in the exhaust duct.*

The remaining processes yield information concerning the composition and state of the fluid at 1.

4-5. The gas remaining in the cylinder at 5 may be assumed to have expanded reversibly and adiabatically as it expelled the gas flowing out through the valve. This process is a continuation of the constant-entropy process 3-4 to a specific volume corresponding to 4' at the pressure of state 5. The ratio of the mass of gas in the cylinder at 5, m_5 , to that at 4, m , is given by

$$\frac{m_5}{m} = \frac{V_4}{V'_4},$$

where V_4 and V'_4 denote the volumes corresponding to states 4 and 4' of Fig. 137.

5-6. The specific volume of the gas in the cylinder at 6 is the same as at 5, which is in turn the same as that corresponding to 4'. Therefore, the ratio of the mass of the unpurged gas at 6, m_6 , to the mass in the cylinder at 1, 2, 3, and 4 is given by

$$\frac{m_6}{m} = \frac{V_6}{V'_4}.$$

It follows that the ratio of the mass of fresh charge, m_f , introduced in process 6-1 to the total mass present in processes 1-2-3-4 is given by

$$\frac{m_f}{m} = 1 - \frac{V_6}{V'_4}.$$

6-1. The mass of fresh charge m_f is mixed with the mass of unpurged gas m_6 at constant pressure. From the First Law the sum of the enthalpies of these two masses before mixing is equal to the enthalpy of the resulting mixture. Thus,

$$m_f h_f + m_6 h'_4 = m h_1,$$

where h_f , h'_4 , and h_1 denote respectively the enthalpies of fresh charge, unpurged gas, and resulting mixture, each per unit mass.

* As is evident from the energy equation of steady flow if kinetic energies at inlet and exhaust are negligible.

Properties of the Fluid of the Internal-Combustion Engine

The preceding analysis is of little value unless we know the magnitudes of the properties employed, and these in turn require complete knowledge concerning the various states of the fluid. To evaluate the change in internal energy ($E_1 - E_2$) we must know the proportions of the gases (and liquid, if any) that constitute the mixture, the properties of the constituents in terms of pressure and density, and the rule (Dalton's Law, for instance) by which the properties of the mixture may be determined from the properties of the constituents.

The identification of state 3, however, introduces some new considerations. The density and internal energy of the fluid at 3 are identical with those at 2, though all other properties — pressure, temperature, etc. — are different as a result of a chemical reaction. Moreover, every point on the line 2-3 denotes a state of the same mass per unit volume and the same internal energy as states 2 and 3. State 3 must, therefore, be selected from among an infinite number of states, all of which satisfy the requirements for density and internal energy.

For analytical purposes it is usually assumed that state 3 is the most stable of all possible states of the system that satisfy the other requirements. To identify the most stable state we must know the *equilibrium constants* for the various reactions that can occur, as explained in Chapter XXVI. The states along the lines 3-4 and 4-4' are treated similarly.

From the values of the equilibrium constants it is found that for the most stable states combustion is most complete at low temperatures; at high temperatures there is an appreciable degree of dissociation. Therefore, in the process 3-4 an appreciable amount of combustion occurs.

Various studies have been made of internal-combustion processes by the methods just outlined. A notable example is the work of Goodenough and Baker,* who obtained among other things the relation between work, compression ratio, and air-fuel ratio for the simplified Otto engine.

More recently Hershey, Eberhardt, and Hottel† have prepared charts giving the properties of mixtures of air and octane gas and of the same material in its most stable states. These charts permit one to make calculations analogous to those of Goodenough and Baker with relative ease.

* "A Thermodynamic Analysis of Internal-Combustion Engine Cycles," *Univ. of Illinois Eng. Exp. Sta. Bull.* 160, 1927.

† "Thermodynamic Properties of the Working Fluid in Internal-Combustion Engines," *S.A.E. Journal*, October 1936, pp. 409-424.

E = TOTAL INTERNAL ENERGY, B T U
 E_s = INT. ENERGY, EXCLUSIVE OF
 INT. ENERGY OF COMBUSTION
 H = TOTAL ENTHALPY, $E + PV$ (144 / 778), B T U
 $H_s = E_s + PV$ (144 / 778), B T U
 P = PRESSURE, LBS / SQ. IN. (DASHED LINES)
 V = VOLUME, CU FT (SOLID LINES)

S = TOTAL EN
 T = TEMPERA
 BASE = 60 °F.
 (SEE TEX
 FUEL = $(CH_{2.2})$

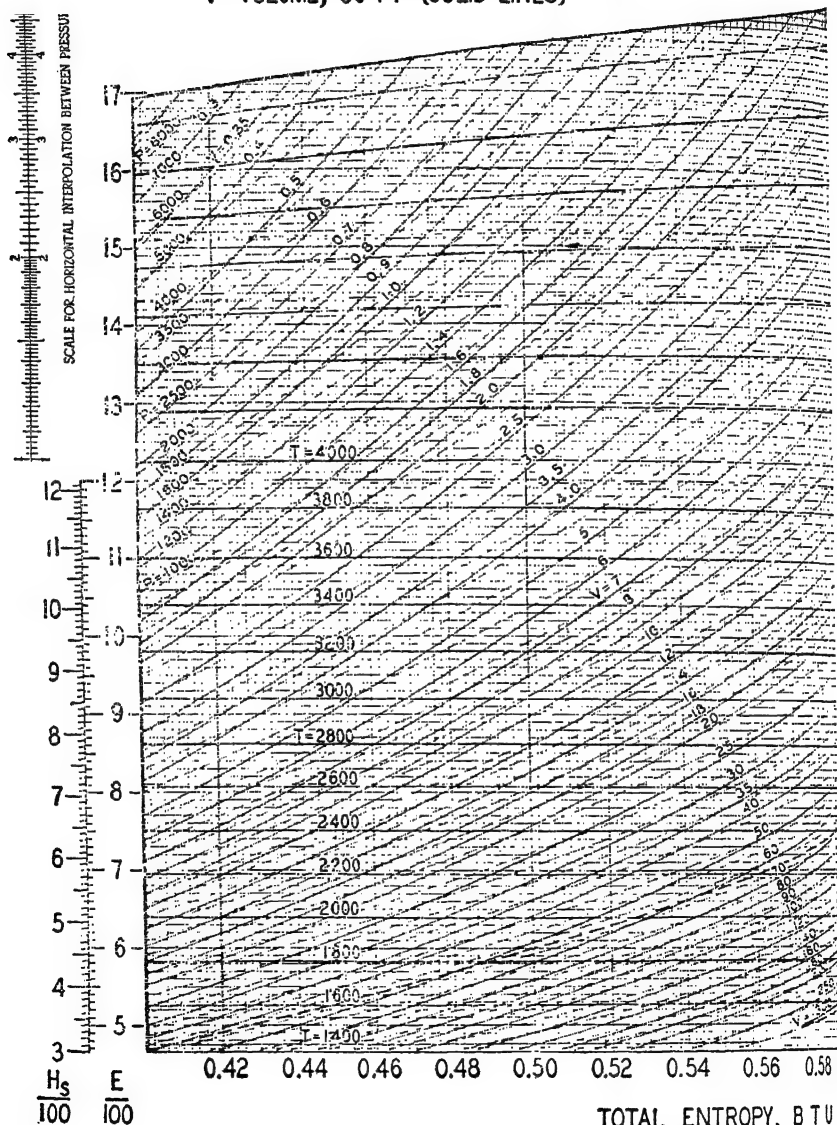
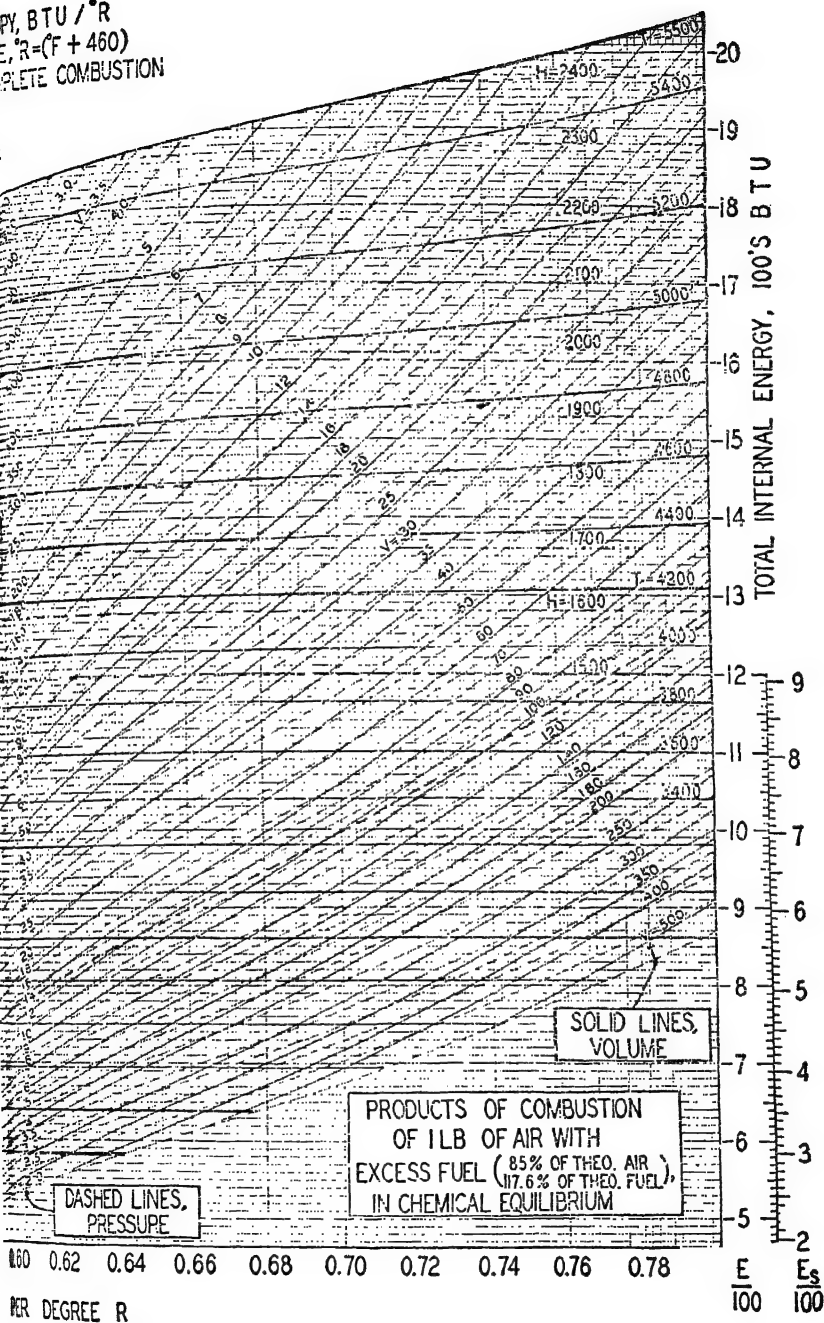


FIG. 139. Pro

From Hershey, Eberhardt, and Hotchkiss

TEMP, BTU / °R
DE, °R = (°F + 460)
COMPLETE COMBUSTION



The chart of internal energy against entropy given by Hershey, Eberhardt, and Hottel for a rich mixture containing 85 per cent of the air required for complete combustion is shown in Fig. 138, and the corresponding chart of most stable states is shown in Fig. 139. The fuel-air mixture of Fig. 138 consists of octane vapor, C_8H_{18} , and air. The products in the most stable states of Fig. 139 consist of CO_2 , H_2O , N_2 , O_2 , CO , H_2 , OH , H , O , and NO in the proportions indicated for each state by measured values of the equilibrium constants for the various reactions involved. At lower temperatures the products of complete combustion, CO_2 and H_2O , will predominate; at higher temperatures, where dissociation sets in, the other molecular species listed above will be present in appreciable quantities.

In evaluating the properties of these mixtures it was assumed that the internal energy and the entropy of the mixture would be the sum of the internal energies and the entropies of each of the constituents existing alone at the temperature and volume of the mixture, as required by the Gibbs-Dalton Law. The internal energy of any mixture was reckoned from that state of the same material in which it consists only of the species CO_2 , H_2O (vapor), O_2 ,* and N_2 , each existing separately at 60 F and 14.7 lb/sq in. abs, at which state the value of zero was assigned. The entropy of the mixture was reckoned in precisely the same way.

The quantities E_s and S_s shown on the charts are respectively the internal energy and entropy reckoned from a reference state in which each of the constituents of the mixture exists separately at 14.7 lb/sq in. and 520 F abs in the same state of chemical aggregation as in the mixture. The internal energy E may be found from E_s by adding to E_s the decrease in internal energy when the system changes at 60 F and 14.7 lb/sq in. abs to a composition consisting only of CO_2 , H_2O , O_2 , and N_2 . The entropy S may be found from S_s by a corresponding addition.

By employing the quantities E_s and S_s it is possible to represent in a single chart, Fig. 138, the properties of a relatively large range of mixtures of air and fuel with unpurged products of combustion. The values of E_s and S_s are affected very little by change in the unpurged fraction of the mixture, though the values of E and S are affected appreciably. The value of E may be found from Fig. 138 by adding to the value of the ordinate the " E of combustion," which is given by

$$1507(1 - f) + 300f,$$

* "The fact that the O_2 content of a rich mixture at this point is negative is immaterial, since the E of O_2 at the base temperature is by definition zero." Hershey, Eberhardt, and Hottel, footnote, p. 411.

where f denotes "the weight fraction of the charge left in the clearance volume." No expression is given in the original paper for the " S of combustion."

Application of the Charts to an Otto-Engine Process

The following example is taken from the paper by Hershey, Eberhardt, and Hottel:

Assume the following:

85 per cent of theoretical air.

Compression ratio = 6.

Intake and exhaust manifold pressures = 14.7 lb/sq in. abs, the fuel-air mixture leaves the carburetor completely vaporized and at 90 F.

Temperature of the mixture of fresh charge and unpurged gas in the cylinder at 1 (Fig. 137) = 190 F or 650 F abs.

Fraction of the gas from the preceding cycle left in the cylinder at 6 (Fig. 137) = 0.05 = f .

The last two assumptions may be verified at the end of the calculation.

Process 1-2. Isentropic compression of the charge.

$p_1 = 14.7$, $T_1 = 650$; from Fig. 138 $E_{s1} = 26$, $S_{s1} = 0.112$, $v_1 = 16.8$.

$E_1 = 26 + 1507(1 - 0.05) + 300 \times 0.05 = 26 + 1447 = 1473$.

Then $v_2 = v_1/6 = 2.8$, and $S_{s2} = 0.112$. From Fig. 138,

$p_2 = 160$, $T_2 = 1158$, $E_{s2} = 138$, $E_2 = 138 + 1447 = 1585$.

$W_{12} = E_1 - E_2 = E_{s1} - E_{s2} = -112$.

Process 2-3. Constant-volume burning.

$v_3 = v_2 = 2.8$, $E_3 = E_2 = 1585$.

From Fig. 139, $S_3 = 0.576$, $p_3 = 770$, $T_3 = 4990$.

Process 3-4. Isentropic expansion.

$v_4 = v_1 = 16.8$, $S_4 = S_3 = 0.576$.

From Fig. 139, $p_4 = 80$, $T_4 = 3300$, $E_4 = 1010$.

$W_{34} = E_3 - E_4 = 1585 - 1010 = 575$.

Process 4-5. The gas remaining in the cylinder at 5 is assumed to have expanded isentropically to atmospheric pressure.

$p_5 = 14.7$, $S_5 = 0.576$.

From Fig. 139, $v_5 = v_4 = 66$, $T_5 = 2300$, $E_5 = 723$, $H_{s5} = 610$. The values of v , E , and H_s for this state and all other states are for a mass of mixture corresponding to 1 lb of air. For each such unit of material in states 1, 2, 3, and 4, only the fraction $v_4/v_5 = 0.255$ of a unit remains in the cylinder at 5.

Process 5-6. Expulsion of the fraction V_6/V_5 of the remaining gas at constant pressure. The fraction of each unit remaining at 6 is, therefore, V_6/v_5 , where V denotes the volume of the confined gas. For each unit present in states 1, 2, 3, and 4 the volume at 6 would be

$$V_6 = v_2 = 2.8.$$

Therefore, the unpurged fraction f at 6 is $2.8/66$ or 0.0424 , as compared with the assumed value 0.05 .

Process 6-1. Mixing of the unpurged fraction f with the fraction $(1 - f)$ of fresh charge at constant pressure. This is a constant-enthalpy process; that is, the enthalpy of the mixture at 1 will be the sum of the enthalpies of the unpurged gas and fresh charge before mixing. Since no chemical combination or dissociation occurs during the process the enthalpies may be reckoned from a reference state at which the chemical composition is the same as in the state in question. Such an enthalpy we shall denote by H_s . Then

$$H_{s1} = fH_{s6} + (1 - f)H_{sm},$$

where H_{sm} denotes the enthalpy of a unit of fresh charge in the state in which it is supplied: 14.7 lb/sq in. abs and 90 F (550 F abs). From Fig. 138, $H_{sm} = 43$; from Fig. 139, $H_{s6} = H_{s5} = 610$. Then

$$H_{s1} = 0.0424 \times 610 + 0.9576 \times 43 = 67.$$

Moreover,

$$p_1 = 14.7.$$

From Fig. 138, $T_1 = 640$, $v_1 = 16.5$, $E_{s1} = 23$, $S_{s1} = 0.105$.

The value assumed for T_1 at the beginning of the calculation was 650 . With the new values of T_1 and f the processes may be recalculated to obtain a closer approximation to the correct values. However, the values found above are good enough for our present purpose.

The net work of the operation, W , is given by

$$W = W_{12} + W_{34} = -112 + 575 = 463 \text{ Btu}$$

for that mass of gas which corresponds to 1 lb of air and to 0.0782 lb of fuel. The displacement volume corresponding to this much fluid is $(v_4 - v_2) = 14$ cu ft. The mean effective pressure is, therefore, given by

$$\text{mep} = 463 \times \frac{778}{14} \times 144 = 178 \text{ lb/sq in.}$$

Only the fraction $(1 - f)$ or 0.9576 of the quantities of air and fuel in the cylinder during the working strokes was introduced during one set of operations: 0.9576 lb of air and 0.0749 lb of fuel. The work done per pound of fuel supplied is, therefore,

$$\frac{463}{0.0749} = 6190 \text{ Btu.}$$

To obtain an efficiency we may divide the work by the maximum possible

work ($Z - Z_{\min.}$) for fuel mixed with the air required for complete combustion. For this quantity we may use 19,800 Btu per pound of fuel.* The efficiency η is then

$$\eta = \frac{6190}{19,800} = 31.2 \text{ per cent.}$$

A more conventional efficiency is that corresponding to the efficiency of a heat-engine power plant: the ratio of work to a heating value of the fuel. If we select a heating value measured in a flow-type calorimeter with sufficient air mixed with the fuel to insure no condensation of water in the products, the denominator becomes the H of combustion per pound of fuel. From the data of Fig. 138 the heating value is $1504/0.0782 = 19,240$ Btu/lb. The efficiency is then

$$\eta = \frac{6190}{19,240} = 32.1 \text{ per cent.}$$

The difference between this and the preceding figure is not of importance; and the performance of internal-combustion engines could be compared adequately on either basis. Since a heating value is more readily measurable than the decrease in Z , the second method is usually preferred.

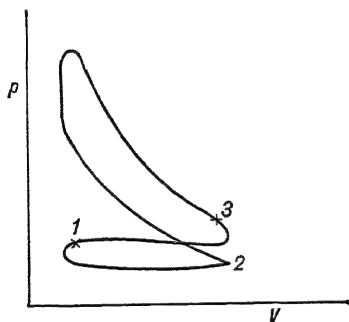


FIG. 140

Analysis of an Indicator Diagram of an Internal-Combustion Engine

Let us analyze the processes in an actual Otto engine corresponding to the indicator diagram of Fig. 140. At 1 the exhaust valve closes and the inlet valve opens; at 2 the inlet valve closes; at 3 the exhaust valve opens.

If we assume all processes to be adiabatic we get for the process 1-2 by familiar methods†

$$(m_f + m_r)e_2 - m_f h_i - m_r e_1 = -A_{12}, \quad [a]$$

where m_r denotes the mass of the residual or unpurged gases at 1, m_f the mass of fluid introduced in the process 1-2, e the internal energy per unit mass, h_i the enthalpy per unit mass of the fluid in the intake manifold, and A_{12} the integral of $p dV$ for the process 1-2. A similar analysis yields the equation

$$(m_f + m_r)(e_3 - e_2) = -A_{23}. \quad [b]$$

* See footnote p. 418, Hershey, Eberhardt, and Hottel.

† See the analysis of an open system, page 32.

From these equations and the conditions

$$m_f + m_r = \frac{V_2}{v_2} = \frac{V_3}{v_3} \quad [c]$$

it is possible to compute the magnitudes m_f , m_r , and the properties corresponding to the states 1, 2, and 3, provided that the state of the mixture in the intake manifold is known.

To do this we shall first assume a value for the temperature t_1 . From t_1 and the value of p_1 obtained from the indicator diagram the state 1 may be identified on a chart of properties of products of combustion. Values of e_1 and v_1 may be obtained from the chart. Then m_r is given by

$$m_r = \frac{V_1}{v_1}. \quad [d]$$

Combining [a], [c], and [d], we get

$$e_2 = \frac{-A_{12} + (V_2/v_2 - m_r)h_i + m_re_1}{V_2/v_2}. \quad [e]$$

The only unknowns in this equation are e_2 and v_2 ; therefore, we may plot a curve of e_2 against v_2 corresponding to equation [e]. The chart of properties permits us to plot another curve of e_2 against v_2 corresponding to the pressure p_2 which may be taken from the indicator diagram. The state 2 is that corresponding to the intersection of these two curves. With the value of v_2 at the intersection we may compute $(m_f + m_r)$ from [c].

Solving [b] for e_3 we get

$$e_3 = \frac{-A_{23}}{m_f + m_r} + e_2.$$

With this value of e_3 and with p_3 taken from the indicator diagram, we may enter the chart of properties of the products and obtain v_3 . According to [c] the value of V_3/v_3 should be identical with that of V_2/v_2 . If it is not, a new value of t_1 must be assumed and the calculation repeated. The solution is complete when a value of t_1 is found for which

$$\frac{V_2}{v_2} = \frac{V_3}{v_3}.*$$

* Any other state of *equilibrium* between 2 and 3 could be substituted for state 3 in this analysis.

An equation similar to [a] may be derived for the adiabatic exhaust process 31. It may be stated in the form

$$h_e = \left(1 + \frac{m_r}{m_f}\right)e_3 - \left(\frac{m_r}{m_f}\right)e_1 - \frac{A_{31}}{m_f},$$

where h_e denotes the enthalpy per unit mass of the fluid in the exhaust manifold when it is homogeneous in state. With this value of h_e and a measured value of the pressure in the exhaust manifold we may enter the chart of properties of the products and find the state of the fluid in the exhaust manifold.

The Internal-Combustion Engine and the Steam Power Plant

In Chapter XII it was pointed out that the efficiency of a steam power plant is limited by the maximum temperature attained by the steam, and that this maximum is in turn limited by the characteristics of the metals from which restraining walls can be made. Thus, there is imposed a "metallurgical limit" which today is a temperature slightly less than 1000 F.

In the example given above, the temperature of the gases in an internal-combustion engine reaches 4990 F abs or about 4500 F at state 3. Temperatures of this order of magnitude have been measured in actual engines. Since the rise in temperature in an internal-combustion engine is not the result of transfer of heat through metal walls, the limiting temperature for successful operation is far higher than that of the steam heat engine. The work produced from a pound of a given fuel is therefore greater (other things being equal) in an internal-combustion engine than in a steam power plant.

We might well inquire then into the reasons why the steam power plant remains the major source of power for every purpose except transportation. The first of these is the fact that the internal-combustion engine can operate successfully only on a relatively refined and expensive liquid fuel. The steam power plant, on the other hand, can readily employ solid fuels as well as the cheapest liquid fuels. Since the difference in price generally exceeds 50 per cent, the efficiency of the internal-combustion engine must be approximately 50 per cent greater than that of the steam plant if it is to be equally economical.

The second reason why the steam power plant continues to flourish is that it can be made in units of larger capacity. The reciprocating type of mechanism employed in the internal-combustion engine can be built in units hardly in excess of 10,000-kw capacity. The steam power plant with its turbine type of mechanism can readily be made for capacities ten to fifteen times as great. Many of the losses or irreversi-

bilities of a power plant vary in importance almost inversely as the capacity of the plant; therefore, the large steam power plant approaches very closely a realization of its full possibilities. Moreover, the cost of manufacture of a large steam power plant is small per unit of capacity as compared with that of the relatively small internal-combustion engine.

Many other considerations, of course, enter into the selection of the type of power plant for any specific purpose. Thus, in short-haul marine traffic the simplicity and ruggedness of the steam plant outweigh considerations of efficiency; in an airplane the small amount of heat-transfer surface required by the internal-combustion engine outweighs almost all other considerations.

The Internal-Combustion Turbine

In the preceding section it was stated that the turbine type of mechanism makes it possible to build steam power plants of great size. Let us consider the problem of adapting the turbine type of mechanism to the internal-combustion engine.

To maintain high efficiency in an internal-combustion engine it is necessary that the air and fuel be compressed before ignition. In the reciprocating engine this is accomplished in a nearly reversible manner by the compression stroke of the piston. In a turbine device of large capacity it would be accomplished by means of a centrifugal compressor. Only at very large capacities would the centrifugal compressor attain the degree of reversibility realized in the compression stroke of the piston of an engine of moderate size. Similar comments might be made concerning the expansion process, though it is easier to make an efficient turbine than it is to make an efficient centrifugal compressor.

The steam power plant employs an expansion turbine and, sometimes, a centrifugal compressor in the form of a feed pump. But here the work of compression is so small compared with the work of expansion that the efficiency of the compressor is of no great consequence. The compressor might absorb twice the work of reversible compression with small effect on the performance of the cycle. A similar condition in an internal-combustion plant might well reduce the efficiency nearly to zero.

Another consideration of first importance is that it is difficult to maintain all the metal parts of a turbine at temperatures below 1000 F where the temperature of the gases streaming by is 4000 F. Unless means can be found to accomplish this, the internal-combustion plant will be subject to the same limitations in temperature as the steam plant, and then the steam plant will be distinctly superior. Various attempts have been made to solve this problem.

An equation similar to [a] may be derived for the adiabatic exhaust process 31. It may be stated in the form

$$h_e = \left(1 + \frac{m_r}{m_f}\right)e_3 - \left(\frac{m_r}{m_f}\right)e_1 - \frac{A_{31}}{m_f},$$

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Today there are in existence only a few internal-combustion engines of the turbine type, because this kind of engine has not yet been perfected to a degree that would make it of general utility. When it is perfected it will have certain of the advantages of the internal-combustion engine and the steam power plant in combination; in particular it will be low in cost per unit of capacity, economical in fuel consumption, and independent of the large supply of cooling water which is necessary to the steam plant. These last two considerations are of military importance in a region exposed to attack from the air.

PROBLEMS

1. Lewis and Randall in *Thermodynamics* give

$$Z - Z_{\min.} = 94,260 \text{ cal/gram mole of C}$$

for the reaction $C + O_2 = CO_2$ at 298 K and 1 atm. For the same reaction to the same end state, they give for the decrease in H 94,250 cal/gram mole of C at the same temperature.

- (a) Find the maximum possible useful work per pound of C.
- (b) Find the heat that can be transferred per pound of C from a steady stream of C and O_2 as a result of combustion which proceeds to the state of maximum stability.
- (c) Find the change in entropy per pound of C which results from reaction to the state of maximum stability.
- (d) Find the maximum useful work per cubic foot of products of combustion at 298 K.
- (e) Find the heat from the steady stream per cubic foot of products of combustion at 298 K.

2. Demonstrate: (a) that for any chemical reaction the condition of minimum H at a given pressure and temperature is not the condition of stable equilibrium; (b) that the change of state from the state of minimum H to that of maximum stability must be endothermic.

3. Consider the combustion of octane, C_8H_{18} , from an initial temperature of 70 F to a final temperature of 70 F at one standard atmosphere. Assume that the most stable state is that corresponding to complete combustion to CO_2 and H_2O and that Dalton's Law of mixtures holds for the products (see Chapter XIII).

- (a) Find the difference per pound of octane between the changes in enthalpy for combustion in the presence only of the minimum oxygen, and for combustion in the presence of so much air that no liquid water is formed.
- (b) If the change in enthalpy is 19,240 Btu/lb of octane for combustion to all vapor, find the enthalpy changes for combustion in the presence of the minimum oxygen, and for combustion in the presence of air containing the minimum oxygen.
- (c) If all the remaining water vapor could be separated from the mixture and condensed under a pressure equal to its partial pressure in the mixture, find the change in enthalpy for this case.

4. Show that the change in Z as the result of a reaction is almost exactly the same whether the H_2O is assumed to be all liquid or part liquid and part vapor at the final temperature.

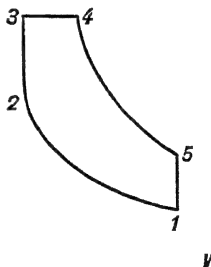
5. Compute the efficiency of the air-standard Otto cycle for a compression ratio of 6, using water vapor ($k = 1.3$), air ($k = 1.4$), and helium ($k = 1.58$).

6. Draw the air-standard Otto and Diesel cycles on a T - s diagram.

7. For an air-standard Otto cycle, find expressions for (a) the ratio of maximum temperature to minimum (atmospheric) temperature, and (b) the ratio of the mean effective pressure to the minimum (atmospheric) pressure in terms of the compression ratio, the heat added per pound of air, and the minimum temperature.

8. For an air-standard Diesel cycle, find the expressions corresponding to (a) and (b) of the preceding problem.

9. The accompanying sketch shows an air-standard cycle known as a limited-pressure cycle. It consists of an adiabatic compression 1-2, heating at constant volume 2-3, heating at constant pressure 3-4, adiabatic expansion 4-5, and cooling at constant volume 5-1. It can be seen that the Otto and Diesel cycles are special cases of the limited-pressure cycle.



(a) Show that the efficiency of this cycle is given by the expression

$$\eta = 1 - \left(\frac{1}{r}\right)^{k-1} \left[\frac{\alpha\beta^k - 1}{(\alpha - 1) + k\alpha(\beta - 1)} \right],$$

where r denotes the compression ratio, α the pressure ratio p_3/p_2 , and β the volume ratio V_4/V_3 .

(b) Show this cycle on a T - s diagram.

10. Justify the statement on page 281 to the effect that

$$H_{s1} = fH_{s6} + (1 - f)H_{sm}.$$

11. In the example given on pages 280 to 282 change the compression ratio in turn to 4 and 8, keeping other things the same. Then find the properties of the various states, the unpurged fraction, and the efficiency. Plot the efficiency against compression ratio.

SYMBOLS

c_v	specific heat at constant volume
e	internal energy of unit system in general
E	internal energy of system in general
E_s	internal energy reckoned from a special reference state
f	unpurged fraction
h	enthalpy per unit mass
\overline{HV}	heating value
k	isentropic exponent

m	mass
p	pressure
q	a positive number representing a quantity of heat
Q	heat to system
r	compression or expansion ratio
S_s	entropy reckoned from a special reference state
S	entropy
T	absolute temperature
v	volume of unit mass
V	volume
W	work
W_u	useful work

GREEK LETTERS

η	efficiency
Z	$(H - TS)$

SUBSCRIPTS

c	compression
e	expansion, exhaust
f	final state, fresh charge
n	net
o	initial state
p	power plant
r	residual gases

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CHAPTER XVII

AVAILABILITY

The First Law states that in every cyclic process either work is converted into heat or heat is converted into work. In this sense it makes no distinction between work and heat except to indicate a means of measuring each in terms of equivalent units. Once this technique of measurement is established, work and heat become entirely equivalent for all applications of the First Law.

The Second Law, on the other hand, marks the distinction between these two quantities by stating that heat from a single source whose temperature is uniform cannot be completely converted into work in any cyclic process, whereas work from a single source can always be completely converted into heat. The efforts of the engineer are very largely directed toward the control of processes so as to produce the maximum amount of work, or so as to consume the minimum amount of it. The success of these efforts can be measured by comparing the amount of work produced in a given process with the maximum possible amount of work that could be produced in the course of a *change of state* identical with that which occurs in the process. In the following paragraphs we shall show how this criterion can be defined and evaluated as a consequence of the Second Law.

(Any system employed by the engineer must operate within an environment, an atmosphere of indefinite extent, which we shall term the *medium*. We shall assume that this medium is in its most stable state: all parts of it are at rest relative to each other, it is homogeneous in temperature and composition, and it is uniform in pressure at any level in the gravitational field. These conditions are necessary to insure that the medium alone, without the aid of a non-cyclic process in a separate system, cannot serve as a source of work.*) We shall assume further that any system employed will always remain distinct from the medium; that is, it must not diffuse into it, dissolve in it, or enter into chemical reaction with it.†

* Work could be produced from motion by a windmill, from difference in temperature by a heat engine, from differences in composition by a diffusion engine, etc.

† This condition does not exclude the possibility of diffusion into or chemical reaction with a limited quantity of air, as in humidification of air or combustion of coal. In such instances the necessary amount of air would be included in the description of the system. Unlimited diffusion into or combination with the *entire medium* must be excluded if any practical result is to be obtained.

If a system within this medium is at rest relative to the medium and is in equilibrium with it as regards pressure, temperature, electricity, and magnetism, then there is no possibility of obtaining work from interaction between the system and the medium. If we further specify that the system itself is in a state of stable equilibrium — that is, there is no tendency toward a change of state that can be made evident by any kind of disturbance — then there is no possibility of obtaining work from the system, from the medium, or from interaction between the two. This state of the system within the medium we shall call the *dead state*.

If the system is in any state other than the dead state it will spontaneously change its condition (given sufficient disturbances) toward the dead state, and this tendency to change spontaneously will vanish only when the dead state is reached. Since the change from any given state to the dead state is spontaneous, no work need be supplied from any source external to the system and medium in order to cause the change. Therefore we may write for a change in the state of the system to the dead state that the maximum value of the work which can be produced by the system and medium is not less than zero, or

$$W_{\max.} \geq 0,$$

where $W_{\max.}$ denotes the maximum useful work — that is, the maximum work which can be delivered to things other than the system and medium. This useful work is not necessarily a product of the system alone, but is the net work produced by the system and the medium. Its maximum value corresponding to any state of the system we shall call the *availability* corresponding to that state. The *availability* may therefore be defined as *the maximum work which can result from interaction of system and medium when only cyclic changes occur in external things except for the rise of a weight*. We shall prove that the availability corresponding to a state of a system for which its energy is E , its volume V , and its entropy S is given by the expression

$$(E + p_0V - T_0S) - (E_0 + p_0V_0 - T_0S_0),$$

where p_0 and T_0 denote respectively the pressure and temperature of the medium (and also the pressure and temperature of the system in the dead state), and E_0 , V_0 , and S_0 denote respectively the energy, volume, and entropy of the system in the dead state.

It is necessary first to prove that, when exchange of heat can occur between system and medium only, the maximum work which can be delivered beyond the boundaries of the medium when the system changes from one state to another is the work which is delivered when the change is in every respect reversible.

Assume that there is a process by which the change in state can occur which results in more work than a reversible process. By definition, there is a process complementary to the reversible process in which all the effects of the reversible process (including the change of state of the system) can be undone. In this complementary process the system will receive an amount of work equal to that it delivers in the reversible process. A cycle can be executed in which the complementary process is the work-receiving part and the assumed process the work-delivering part. By assumption, a net amount of work will be delivered to things other than the system and medium. Since the system can receive heat from the medium only, it follows that it constitutes a machine which can continuously deliver work at the expense of a single source of heat, namely, the medium. According to the Second Law, such a machine is impossible. Therefore, no process which can be executed between two states will result in more work than a reversible process. It can be shown in similar fashion that all reversible processes between the same two states will deliver the same amount of work.

Next let us determine the amount of work delivered in the course of a reversible process during which the system changes from state 1 to state 2. Let dQ denote the heat that flows to the system during any infinitesimal step in

this process (dQ being greater than zero if heat flows to the system and less than zero if heat flows from it). For this flow of heat to be reversible without the interference of any substance that suffers a permanent change of state, it is necessary to interpose a reversible engine, working in cycles, between the system and the medium (Fig. 141). The work delivered by this engine for this step in the process is

$$\frac{T_0 - T}{T} dQ,$$

where T denotes the temperature of that part of the system which receives the heat dQ and T_0 the temperature of the medium. The quantity $\left[\frac{T_0 - T}{T} dQ \right]$ is always greater than zero because dQ and $(T_0 - T)$ must be both greater than zero or both less than zero. The work delivered by the engine is not, however, the only work delivered during the step in question. The system may do work by virtue of motion of its boundaries, change in area of surfaces of separation, flow

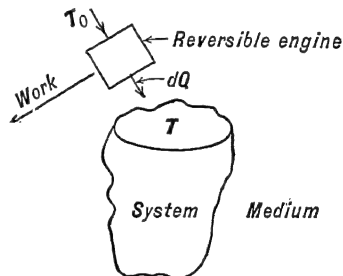


FIG. 141

of electricity through a potential difference, etc. However, any change dV in the volume of the system is resisted by the medium with the pressure p_0 . Therefore, of the work done by the system the amount which can be received by things other than the medium is given by

$$dW - p_0 dV,$$

where dW denotes the total work of all kinds done by the system.

Now the net work delivered is

$$\frac{T_0 - T}{T} dQ + dW - p_0 dV.$$

Substituting dE for $(dQ - dW)$ in the expression for the net work delivered, we get

$$-dE - p_0 dV + T_0 \frac{dQ}{T},$$

or, since the process is reversible,

$$-dE - p_0 dV + T_0 dS.$$

In each step of a process, then, the maximum possible amount of work that can be delivered is equal to the decrease in the quantity

$$E + p_0 V - T_0 S.$$

It follows that for any state of the system the availability is the maximum possible decrease in the quantity $(E + p_0 V - T_0 S)$ if the system exchanges heat with the medium alone. It was shown above that when the system changes from any state to the dead state the maximum amount of useful work from the process is never less than zero, and may be greater than zero. Therefore, the maximum possible useful work will be realized if the system changes reversibly to the dead state, for, if the change should cease at any other state, there might still be the possibility of adding to the work (and there is no possibility of subtracting from it) by proceeding reversibly to the dead state. Employing the subscript 0 for properties of the system at the dead state, we get for the availability corresponding to a state of the system for which its energy, volume, and entropy are E , V , and S respectively

$$(E + p_0 V - T_0 S) - (E_0 + p_0 V_0 - T_0 S_0).^* \quad [145]$$

* From the preceding discussion it follows that $(E_0 + p_0 V_0 - T_0 S_0)$ is the lowest possible value that the property $(E + p_0 V - T_0 S)$ can have. This proposition is proved again in Chapter XXIV.

If we apply [145] to a process in which the state of the system changes from 1 to 2, we get for the increase in availability

$$(E_2 + p_0 V_2 - T_0 S_2) - (E_1 + p_0 V_1 - T_0 S_1), \quad [146]$$

a quantity which will be less than or equal to zero unless work or heat is supplied to the system from some source other than the medium.

The quantity $(E + p_0 V - T_0 S)$ is evidently a property: its value is fixed by the state of the system for any given values of p_0 and T_0 . It should be noted, however, that E denotes the internal energy in its most general sense and comprises kinetic energy, potential energy in a gravitational field or in an electrical field, capillary energy, etc.

Evaluating Irreversibility

The work done during any process by a system which is enclosed in a medium is the sum of the useful work of that process and the work expended on the medium. For any infinitesimal change of state during which the volume of the system increases by dV , the work expended on the medium is $p_0 dV$. Letting dW_u denote the useful work for this change of state, we may, therefore, write [2] in the form

$$dQ = dE + p_0 dV + dW_u.$$

Transposing, and subtracting $T_0 dS$ from both sides of the equation, we get

$$(dE + p_0 dV - T_0 dS) = dQ - T_0 dS - dW_u, \quad [147]$$

which is an expression for the increase in the availability when the work dW_u is delivered to things other than the system and medium.*

The quantities dQ and dS in [147] are related through the Clausius inequality,

$$dS \geq \frac{dQ}{T},$$

which when substituted into the right-hand member of [147] yields the inequality

$$dE + p_0 dV - T_0 dS \geq dQ \frac{T - T_0}{T} - dW_u. \quad [148]$$

The sign of equality holds, as in the Clausius inequality, for reversible processes; the inequality for all others.

* Of course, dW_u may be considered in the algebraic sense: thus, $-dW_u$ denotes work received from things other than the system and medium.

It appears from [148] that when the heat dQ is delivered to a system at temperature T while the system delivers the useful work dW_u the increase in availability may be equal to or less than the quantity

$$dQ \frac{T - T_0}{T} - dW_u.$$

This quantity is, therefore, the maximum possible increase in availability for the process in question, and it is identical with the increase in availability if the process is reversible. The amount by which the maximum possible increase in availability exceeds the actual increase may be used as a quantitative measure of irreversibility. Thus, we may write

$$d(\text{Irreversibility}) = \left[dQ \frac{T - T_0}{T} - dW_u \right] - d[E + p_0 V - T_0 S] \geq 0. \quad [149]$$

In the integrated form we have

$$\text{Irreversibility} = \left[\int \frac{T - T_0}{T} dQ - W_u \right] - \Delta[E + p_0 V - T_0 S], \quad [150]$$

where Δ denotes an increase (in the algebraic sense) in the quantity in parenthesis.

In the above derivation the inequality [148] is obtained from the equality [147] by introducing the inequality

$$T_0 dS \geq T_0 \frac{dQ}{T}. \quad [151]$$

It follows that the departure from equality in [148] must be identical with that in [151], so that we may write

$$\begin{aligned} d(\text{Irreversibility}) &= T_0 dS - T_0 \frac{dQ}{T} \\ &= d(T_0 S) - T_0 \frac{dQ}{T}, \end{aligned}$$

and

$$\text{Irreversibility} = \Delta(T_0 S) - T_0 \int \frac{dQ}{T}. \quad [152]$$

This last expression is simpler than [150] and is sometimes easier to use, but it does not show so clearly the nature of the quantity called irreversibility.

If we apply [150] to an adiabatic process, we learn that the irreversibility is the excess of the work received from things other than the

medium ($-W_u$) over the increase in availability. (If useful work is delivered instead of received, then the irreversibility is the excess of the decrease in availability over the useful work.)

If heat is supplied to the system and W_u is zero the irreversibility is the excess of $[(T - T_0)/T] dQ$ over the increase in availability for the corresponding step in the process. A flow of heat dQ to the system at temperature T is entirely equivalent in this respect to a flow of useful work equal to the work that would be produced from the heat dQ by a reversible cyclic engine working between T and T_0 .

Availability in Steady Flow

The conclusions reached above can be applied to problems in steady flow. Consider a steady stream of fluid entering an apparatus in a state in which its energy, volume, and entropy per unit mass are e_1 , v_1 , and s_1 respectively and leaving it in a state in which the magnitudes of the same properties are e_2 , v_2 , and s_2 .

The availability of each unit of mass of the entering stream with respect to an infinite medium at pressure p_0 and temperature T_0 is now augmented by the amount of work which could be delivered by virtue of the flow: that is, the displacement work $p_1 v_1$ less the work which must be expended on the atmosphere $p_0 v_1$. For, if one imagines the apparatus following section 1 (Fig. 142), corresponding to subscript 1, replaced by a piston closing the passage with pressure p_0 exerted outside and pressure p_1 inside, then for each unit of mass which passes section 1 the amount of work $p_1 v_1$ is done by the fluid on the piston. Of this work the amount $(p_1 - p_0)v_1$ can be delivered to things other than the medium. The unit mass is still in the state corresponding to e_1 , v_1 , and s_1 and may be removed in an appropriate container and caused to deliver at most the amount of work

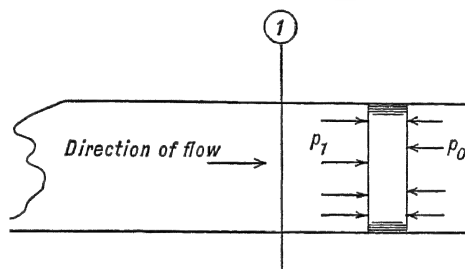


FIG. 142

the apparatus following section 1 (Fig. 142), corresponding to subscript 1, replaced by a piston closing the passage with pressure p_0 exerted outside and pressure p_1 inside, then for each unit of mass which passes section 1 the amount of work $p_1 v_1$ is done by the fluid on the piston. Of this work the amount $(p_1 - p_0)v_1$ can be delivered to things other than the medium. The unit mass is still in the state corresponding to e_1 , v_1 , and s_1 and may be removed in an appropriate container and caused to deliver at most the amount of work

$$(e_1 + p_0 v_1 - T_0 s_1) - (e_0 + p_0 v_0 - T_0 s_0).$$

Addition of these quantities gives the maximum work which a unit mass of fluid in steady flow can deliver, namely,

$$e_1 + p_1 v_1 - T_0 s_1 - (e_0 + p_0 v_0 - T_0 s_0).$$

If the kinetic energy, corresponding to motion relative to the environment, is expressed as $V_1^2/2g$, per unit mass of fluid, then

$$e_1 = u_1 + \frac{V_1^2}{2g},$$

and the expression for maximum work becomes

$$h_1 - T_0 s_1 + \frac{V_1^2}{2g} - (h_0 - T_0 s_0),^*$$

or

$$b_1 + \frac{V_1^2}{2g} - b_0,$$

where

$$b = h - T_0 s.$$

The effect on availability of position in a gravitational field of constant strength g can be included in the expression for the steady-flow case. If the stream passes from level 1 to datum 0 reversibly and adiabatically (that is, isentropically) it can be restored at the new level to a state identical with that at level 1 by an isentropic change in a reversible and adiabatic engine or compressor. According to the energy equation of steady flow [6] the work delivered by the system will be $(z_1 - z_0)$ if a unit force gives a unit mass the acceleration g corresponding to the strength of the gravitational field. Now the fluid may be removed from the steady-flow system and brought into equilibrium with its environment. By addition the availability is

$$b_1 + z_1 + \frac{V_1^2}{2g} - (b_0 + z_0).^\dagger$$

* The availability in steady flow may be negative if the pressure of the substance is less than the pressure of the atmosphere. In the more general case of the closed system (which corresponds to Gibbs' analysis, Chapter XXIV) the availability can never be negative. The requirement that steady flow must be maintained does not permit establishment of equilibrium between the atmosphere and any part of the system without first separating that part from the steady-flow remainder. The separation sometimes involves a work input which can result occasionally in a negative availability.

† A derivation follows which is independent of the energy equation of steady flow for the effect of gravity. Let a unit mass of fluid be withdrawn from the steady-flow system at level 1 instead of at level 0. The work which can be delivered to things outside the flow system other than the medium is

$$(p_1 - p'_0)v_1,$$

where p'_0 is the pressure of the medium at level 1. Now the piece of fluid can be

The decrease in availability per unit mass of fluid between section 1 and section 2 along the path of steady flow is evidently

$$\left(b_1 + z_1 + \frac{V_1^2}{2g}\right) - \left(b_2 + z_2 + \frac{V_2^2}{2g}\right). \quad [153]$$

The amount by which this decrease exceeds the work delivered to things outside the steady-flow system is a measure of the irreversibility of any adiabatic process between 1 and 2.

If two or more streams enter an apparatus, as in a feed-water heater of a power plant, the increase in availability is

$$\sum \left[w \left(b_2 + z_2 + \frac{V_2^2}{2g} \right) \right] - \sum \left[w \left(b_1 + z_1 + \frac{V_1^2}{2g} \right) \right], \quad [154]$$

where w denotes the mass rate of flow of each stream, subscripts 1 and 2 refer respectively to inlet and outlet, and \sum denotes a summation over all streams. Even if one stream dissolves or partially dissolves in the other, or if the streams react chemically with one another, the change in availability can be found from [154]. Of course the values for b must be known for the initial and final states, and this usually means that the values of enthalpy and entropy must be known.

For engines the ratio of work delivered to decrease in availability, $W_x/(-\Delta b)$ (neglecting changes in height and velocity), was proposed by Darrieus for purposes of comparison. Later it was called the effectiveness* to distinguish it from the efficiency, which is defined as the ratio of the work delivered to the isentropic decrease in enthalpy, $W_x/(-\Delta h_s)$.

lifted to level 0 while the amount of work

$$(z_1 - z_0) \left(1 - \frac{v_1}{v_a} \right)$$

(in which v_a denotes the specific volume of the medium, and v_1/v_a allows for the buoyant action of the medium) is delivered to things other than the medium. The availability is then

$$e_1 + p_0 v_1 - T_0 s_1 + (p_1 - p'_0) v_1 + (z_1 - z_0) \left(1 - \frac{v_1}{v_a} \right) - (e_0 + p_0 v_0 - T_0 s_0).$$

Because of the gravitational field

$$p'_0 = p_0 - \frac{z_1 - z_0}{v_a}$$

Substitution results in the expression given above.

* *Mechanical Engineering*, Vol. 54 (1932), pp. 195-204.

Irreversibility in Steady Flow

By an analysis which parallels that given above for a closed system it can be shown that the irreversibility in a steady-flow process is given by the expression

$$\text{Irreversibility} = \left[\int \frac{T - T_0}{T} dQ - W_x \right] - \Delta \left(b + \frac{V^2}{2g} + z \right), \quad [155]$$

where Δ denotes the increase (in the algebraic sense) in the quantity in parenthesis between two successive sections across the path of flow and dQ denotes a heat transfer to the system at temperature T during the time required for unit mass to cross one of the sections. The integral denotes a summation over all such transfers of heat between the two sections.

Changes in Availability in a Rankine Cycle

A simple reversible Rankine cycle is shown as *ONMO* on the h - s and b - s diagrams of Fig. 143. The temperature of condensation is, in this ideal case, identical with T_0 . We shall assume that changes in height and in kinetic energy between the various states are negligible so that the increase in availability between two states 1 and 2 is simply

$$b_2 - b_1.$$

For any isentropic process the change in b (which is, by definition, $h - T_0s$) is identical with the change in h because the change in T_0s is zero. Therefore, in the isentropic expansion *NM*, the work, W_e , delivered in steady flow is given by both the decrease in h and the decrease in b :

$$W_e = h_N - h_M = b_N - b_M.$$

If the expansion ends within the two-phase region no change in b will occur during condensation, because at T_0 the changes in h and in T_0s at constant pressure are both equal to the heat of a reversible process and are, therefore, identical. In the feed pump the process is an isentropic compression so that the pump work, W_p , is given by

$$W_p = h_0'' - h_0' = b_0'' - b_0',$$

where superscripts '' and ' refer to the states at discharge and suction respectively. (These states are too close together to be distinguished from each other in Fig. 143.) The constant-pressure process *ON* which occurs in the steam generator results in an increase in h equal to the heat added, and a smaller increase in b .

Since b is a property (for a fixed value of T_0) the sum of the changes in its value is zero for any cyclic process. In this cycle, therefore, the

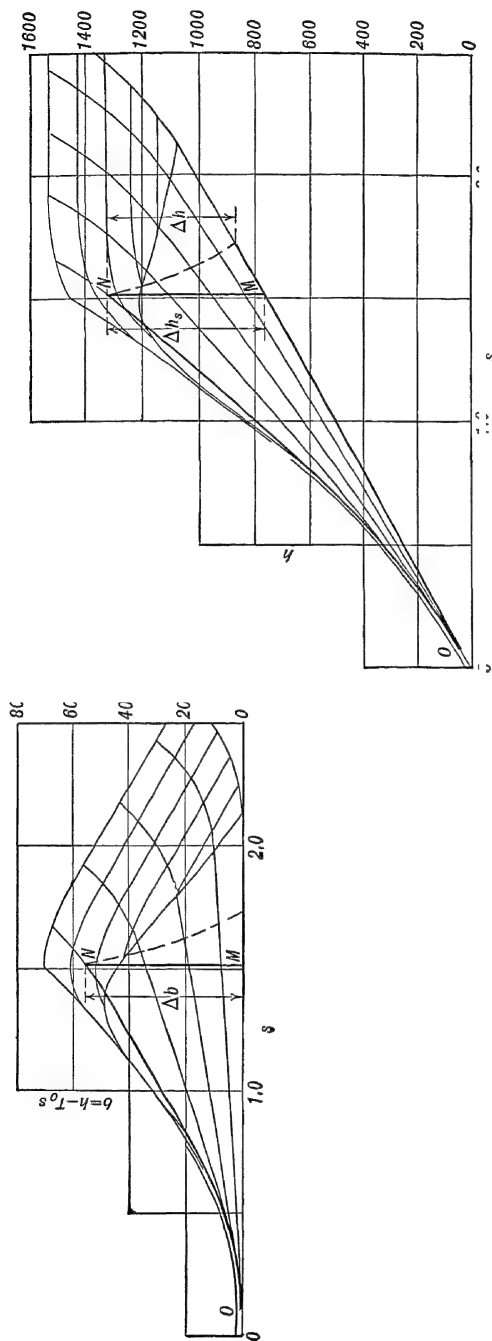


Fig. 143. Simple Power-Plant Cycles, Reversible and Irreversible

From Keenan, *Mechanical Engineering*, Vol. 54 (1932), p. 199.

decrease in b in the expansion process is exactly equal to the increase in b in the compression and heating processes.

The same will be true even if the expansion process is irreversible (as shown by the dash lines of Fig. 143), provided only that the end of the expansion is a two-phase state, for all two-phase states at temperature T_0 have the same value of b . Despite the fact that the decrease in availability is in this instance independent of irreversibility, the work of the expansion process (which is equal to the decrease in h) is appreciably reduced as the irreversibility increases. For the irreversible expansion we may, therefore, write

$$W_e = -\Delta h < -\Delta b.$$

The magnitude of the irreversibility could be expressed as

$$(-\Delta b) - W_e \quad \text{or as} \quad T_0 \Delta s$$

(in accordance with [155] and [152] respectively).

The efficiency, η , of the expansion engine or turbine is defined as

$$\frac{W_e}{-\Delta h_s}$$

where $-\Delta h_s$ denotes the decrease in enthalpy at constant entropy from N to the condenser pressure. The effectiveness, ϵ , on the other hand, is defined as

$$\frac{W_e}{-\Delta b}.$$

For the case in question η and ϵ are identical.

Effectiveness and Efficiency of a Turbine Stage

In Fig. 144 are shown h - s and b - s diagrams for two turbine stages: the upper diagrams for a high-pressure stage, the lower for a low-pressure stage. Let us consider the high-pressure stage. If we neglect changes in kinetic energy across the stage we get for the work delivered to the turbine shaft

$$W_x = \nabla h.$$

(In this equation and in those that follow we shall use the symbol ∇ to denote a *decrease* in the property indicated.) If the process were isentropic (MQ), the work would be identical with the decrease in availability because

$$\nabla h_s = \nabla b_s.$$

In the actual process MP , however, the work is less than the decrease in availability, because the decrease in availability is the work that would be produced in a reversible change between the end states of the actual process. Therefore,

$$\nabla h < \nabla b.$$

Moreover, ∇b must be less than ∇b_s , because in a reversible process,

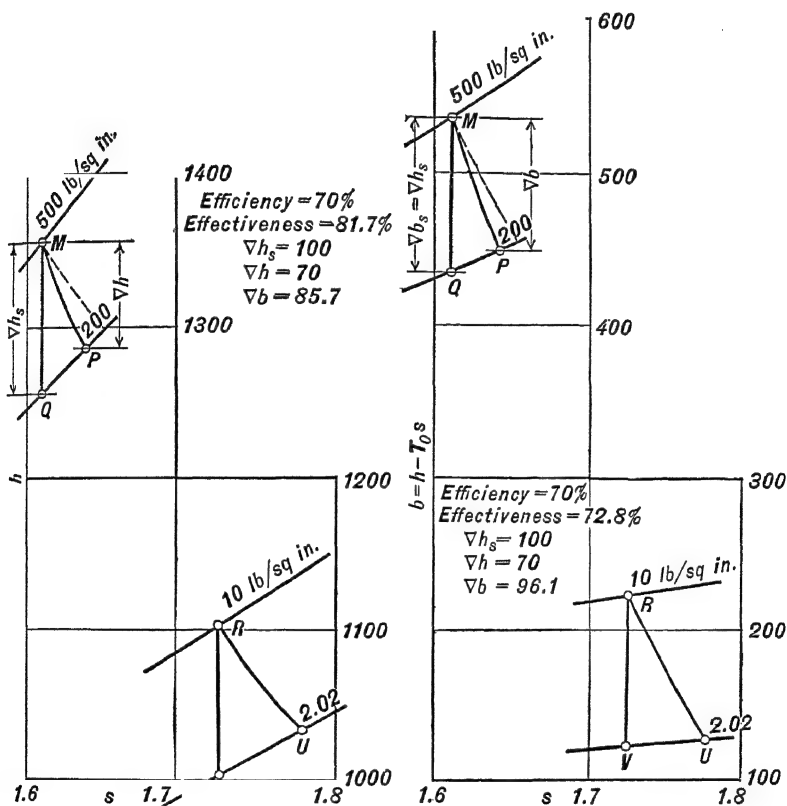


Fig. 144. A High-Pressure Turbine Stage Compared with a Low-Pressure Stage

Though the efficiencies are the same, the effectivenesses are quite different. The stage represented by the broken line between 500 lb per sq in. and 200 lb per sq in. has the same effectiveness as the low-pressure stage. From Keenan, *Mechanical Engineering*, Vol. 54 (1932), p. 199.

PQ , some work would be delivered if the environment at T_0 were used as a reservoir, and the work for the reversible process MPQ must be identical with that for the isentropic reversible process MQ . We may write, therefore,

$$\nabla h_s = \nabla b_s > \nabla b > \nabla h.$$

Furthermore,

$$\frac{W_s}{\nabla b} > \frac{W_s}{\nabla h_s},$$

or

$$\epsilon > \eta.$$

It may seem paradoxical that an irreversible engine operating between M and pressure QP causes less loss in availability than a reversible engine operating between the same limits. Yet therein lies the basic concept of the reheat factor, namely, that by virtue of the irreversibility between M and P the availabilities in stages subsequent to P are increased, and the change in availability between M and QP is correspondingly decreased. We may say, then, that the effectiveness exceeds the efficiency because the effectiveness includes the so-called reheat effect.

The low-pressure stage of Fig. 144 has values of ∇h_s and ∇h identical with those of the high-pressure stage. It follows that the quantities of work, and also the efficiencies, of the two stages are identical. However, the decrease in availability ∇b in the actual process is more nearly equal to ∇b_s in the low-pressure stage than in the high-pressure stage, because the heat from a reversible cooling process UV would flow at such a low temperature that little work could be obtained from it. We find, therefore, that the decrease in availability in the low-pressure stage is greater than in the high-pressure stage and the effectiveness is correspondingly less. The magnitudes of the quantities in question are as follows:

	∇h_s	∇h	∇b	η	ϵ	Irreversibility
High-pressure stage	100	70	85.7	70%	81.7%	15.7
Low-pressure stage	100	70	96.1	70%	72.8%	26.1

From these data it may be seen that low efficiency can be better tolerated in a high-pressure stage than in a low-pressure one. By working this problem backward it can be shown that the efficiency of the high-pressure stage could be reduced to 58.2 per cent before its effectiveness and its irreversibility would equal those of the low-pressure stage of 70 per cent efficiency.

As a measure of the performance of a turbine as a whole the effectiveness has some advantages as compared with the efficiency. The ideal engine implied in the denominator of the definition of the effectiveness may be considered to work along the condition curve of the actual engine, whereas that implied in the definition of efficiency works along an entirely different path, namely, an isentropic path extending from the initial state to the final pressure. Either of these alternatives has a logical basis if the fluid leaving the turbine is a mixture of liquid and

vapor; but if it is a superheated vapor the effectiveness alone can be justified logically.

In Chapter XI it is shown that the overall efficiency of a multistage turbine in which all stages have the same efficiency is distinctly greater than the efficiency of the individual stages. On the other hand, the overall effectiveness of a turbine in which all stages have the same effectiveness is identical with the effectiveness of the individual stages. Moreover, the overall effectiveness of a turbine having stages with various values of the effectiveness is the weighted mean (weighted on the basis of decrease in availability) of the values of the effectiveness for the individual stages; thus

$$\epsilon = \epsilon_1 \frac{\nabla b_1}{\nabla b} + \epsilon_2 \frac{\nabla b_2}{\nabla b} + \quad [156]$$

where the symbols without subscripts refer to the turbine as a whole and those with subscripts refer to individual stages.

A corollary of the preceding paragraph is that the condition curve of a turbine having uniform stage effectiveness is a straight line on the h - s chart and on the b - s chart.

Second-Law Analysis of a Reheating and Regenerative Steam Cycle

A power-plant cycle, more complex than the Rankine cycle, is analyzed in Fig. 145. In this example the availability of the fluid increases as it passes through feed pumps, economizer, boiler, superheater, and reheater; and the availability of the fluid decreases as it passes through turbines, condenser, feed-water heater, valves, and piping. Only in the turbine is the decrease in availability compensated by the production of work, and there it is only partly compensated.

The increases in availability in economizer, boiler, superheater, and reheater are caused by a flow of heat to the fluid; the increase in the pump, on the other hand, is caused by a flow of work and is therefore larger per unit of energy supplied. The decrease in availability in the turbine is caused by the production of work and by friction. The decreases occurring in piping and valves are caused primarily by friction. They have been assumed to be negligible in this instance. The decreases occurring in condenser and feed-water heater are caused by transfer of heat across finite intervals of temperature. The transfer of heat from the condensing vapor at 79 F to the environment at 50 F (corresponding to T_0) results in a loss in availability of 7.7 per cent of the total increase that occurs in pumps, boiler, superheater, and reheater. The transfer of heat from extracted steam to feed water results in a loss of 3.6 per cent

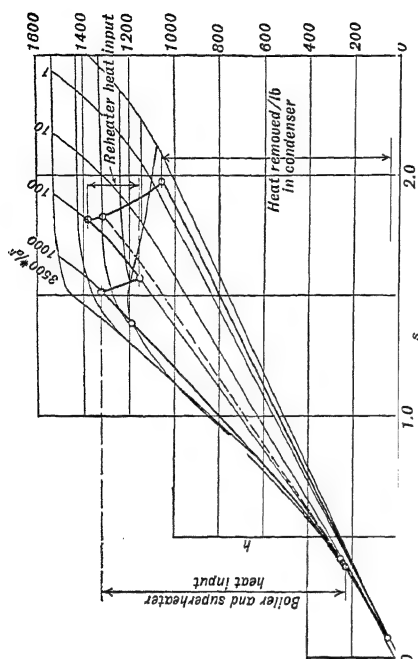
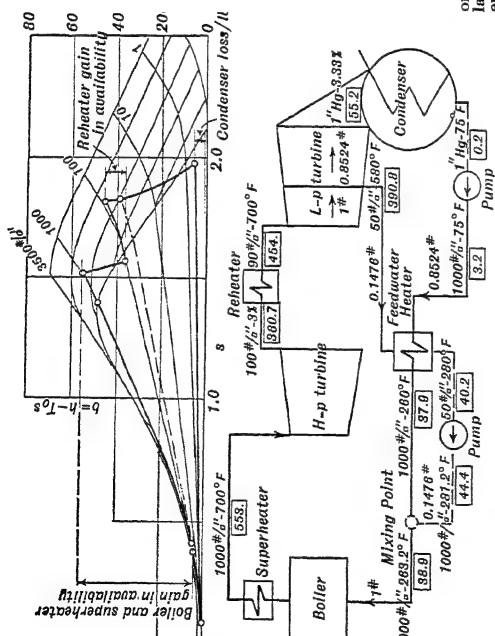


FIG. 145. Reheating Regenerative Cycle

From Keenan, *Mechanical Engineering*, Vol. 54 (1932), p. 199. (Figures in boxes on the diagram of the power plant are the values of b at those points. The calculated results are all per pound of steam entering the turbine. See availability and energy tables below.)

ENERGY INPUT (or Heat Added + Work Added) = $(\dot{Q}_{in})_{out} - (\dot{W}_{in})_{in}$	Btu	Work Efficiency per cent
Energy Input:		
Main feed pump: 0.8524 (46.0 — 43.0)	= 2.6	
Drip pump: 0.1476 (253.2 — 249.0)	= 0.6	
Boiler and superheater: 1324.9 — 234.8	= 1090.1	
Reheater: 1378.7 — 1160.0	= 218.7	
Total energy input	1312.0	
Heat input.....	1308.8	
Energy Output:		
HP turbine: 1160.0 — 1324.9	= -164.9	79.4
Extraction point: 1321.6 — 1378.7	= - 57.1	82.2
LP turbine, extraction point to exhaust: 0.8524 (1060.0 — 1321.6)	= -253.0	77.0



	— (VOLUME —	Per cent of total
Increases in Availability:	Btu	%
Main feed pump; 0.8524 (3.2 - 0.2)	2.6	0.42
Drip pump; 0.1476 (44.4 - 40.2)	0.6	0.10
Boiler and superheater; 553.1 - 38.9	514.2	84.19
Reheater; 454.1 - 360.7	93.4	15.29
Total	610.8	100.00
Decreases in Availability:		
H _p turbine; 360.7 - 553.1	-192.4	31.50
L _p turbine to extraction point; 380.8 - 454.1	- 63.3	10.36
H _p turbine, extraction point to exhaust; 0.3524 (55.3 - 380.8)	-298.0	48.83
C _p turbine; 0.8524 (55.3 - 55.2)	- 40.9	7.08
Extraction heater; (0.8524 × 37.9 + 0.1476 × 40.2) - (0.1476 × 380.8 + 0.8524 × 3.2) = 38.26 - 60.45	- 22.2	3.63
Mixing point	— 610.8	100.00
Total		net usable

of the total increase. There is a further loss due to equalization of temperatures at the point where the drip from the heater joins the main feed line, but it is too small to appear in the first decimal place.

Second-Law Analysis of an Ammonia-Absorption Cycle

The ammonia-absorption refrigeration cycle (Fig. 146), which was analyzed from the standpoint of the First Law in the chapter on refrigeration, is analyzed from the standpoint of the Second Law in Table V. The values of the property b shown in the table were obtained from charts given by Warburton.* The increase in availability in each piece of apparatus was found by means of [154] and the irreversibility by means of [155].

It will be seen from the table that the largest irreversibility occurs in the rectifier. It is in the main the result of transfer of heat across large intervals of temperature. The next largest occurs in the absorber and is principally the result of the mixing of two streams that are not in

TABLE V

SECOND-LAW ANALYSIS OF AMMONIA-ABSORPTION CYCLE (FIG. 146)

The symbols in the column headed *Section* refer to the corresponding sections of Fig. 146.

The quantities given below are the number of Btu's for the period of time required for 1 lb of NH_3 to pass section 1.

$T_0 = 540^\circ\text{F abs } (80^\circ\text{F})$.

Section	b Btu/lb		Heat Received	Work Delivered	Increase in Availability	Irreversibility
1	-7.7	Condenser	-488.5	0	-8.5	-0.4
2	-16.2	Expansion				
2a	-24.8	valve	0	0	-8.6	8.6
3	-95.6	Evaporator	471.4	0	-70.8	0.6
4	-42.7	Absorber	-870.5	0	-94.3	94.3
4a	-43.1	Pump	0	-2.2	2.2	0
5	-70.1	Solution valve	0	0	-0.4	0.4
6	-69.7	Exchanger	0	0	-85.3	85.3
7	-49.3	Still	1770	0	493.5	27.0
8	1.5	Rectifier	-885	0	-226.3	211.7
9	119.3					
10	1.5	Summation ¹	-1.6	-2.2	+1.5	427.5

¹ The heat and work summations should be identical. The summation of the increases in availability should be zero. The total irreversibility should be identical with the summation of $(-T_0 Q/T)$. The small departures from these conditions are the results of inaccuracies in the computations and in the available data on properties.

* T. Warburton, master's thesis, M.I.T., 1938.

equilibrium with each other (they depart from equilibrium as regards temperature and as regards the tendency to dissolve one in the other). Irreversibility in the expansion valve is of the familiar throttling type.

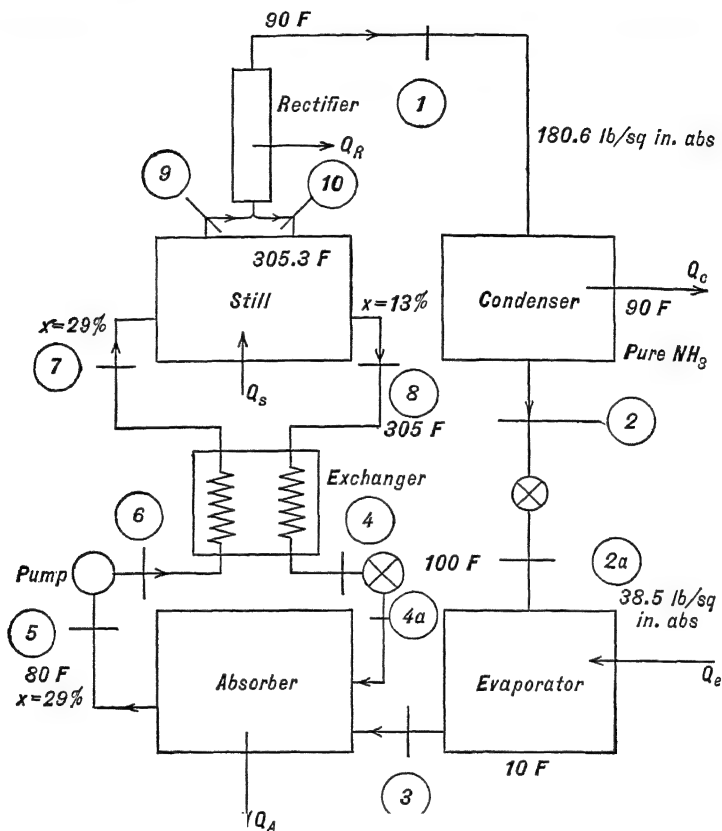


FIG. 146. Ammonia Absorption Cycle

Second-Law Analysis of an Idealized Otto-Engine Process

The processes in an Otto engine will serve to illustrate the application of the Second Law to problems that are not limited to conditions of steady flow.

Consider the operation of an Otto engine which is supplied with octane (C_8H_{18}) mixed with air in the so-called "theoretical" proportions, and make the following assumptions: compression ratio = 6; pressure in the exhaust and intake manifolds = $14.7\text{ lb/sq in. abs}$; temperature in the intake manifold = 90 F or 550 F abs ; pressure in the cylinder during the suction and exhaust strokes = $14.7\text{ lb/sq in. abs}$; isentropic com-

pression and expansion between dead-center positions, constant-volume burning, states after combustion are the most stable states and correspond to those on the Hershey, Eberhardt, and Hottel* chart labeled "Products of Combustion 1 Lb. of Air with the Theoretical Fuel"; temperature of the sink (the atmosphere) = 520 F abs.

The indicator card for this engine is shown in Fig. 147, where the numbers denote the states corresponding to the various events. These states were identified by computations similar to those of the example given by H. E. & H., and restated in Chapter XVI, and the resulting values of the properties are given in Table VI. The unpurged fraction remaining in the cylinder at state 6 proves p to be 4 per cent.

The symbols in the column headed *State* refer to the states indicated in Fig. 147, except that 6' refers to the state of the fluid in the intake manifold, 5'' to that of the fluid in the exhaust manifold which is discharged from the cylinder in the process 4-5, and 6'' to that of the fluid in the exhaust manifold which is discharged in the process 4-6. For purposes of analysis it is assumed that the fluid discharged in process 4-5 reaches a homogeneous state in the exhaust manifold before it mixes with fluid that precedes or follows it. The state 6'' is the state of a homogeneous mass comprising all the exhaust from the engine.

The H. E. & H. chart for the fuel-air mixture before combustion is based on a reference state in which each of the constituents of the mixture exists separately at 14.7 lb/sq in. and 520 F abs in the same state of chemical aggregation as in the mixture. The chart for the products, on the other hand, is based on a reference state in which the entire mass consists of the species H_2O , CO_2 , O_2 , and N_2 , each existing separately at 14.7 lb/sq in. and 520 F abs. In order to compute changes in availability it is necessary to have values of the enthalpy and entropy for all states relative to the same reference state. The reference state of the chart for the products was chosen to be the common reference state, so that values taken from that chart were unaltered. In order to correct to the same bases the values taken from the chart for the fuel-

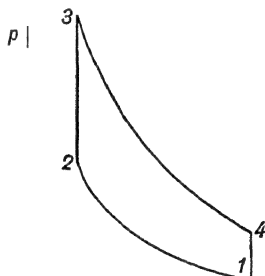


FIG. 147

* "Thermodynamic Properties of the Working Fluid in Internal-Combustion Engines," *S.A.E. Journal*, Vol. 39 (1936), pp. 409-424. In the following paragraphs this paper and its charts will be indicated by the initials H. E. & H.

air mixture it was necessary first to determine the changes in internal energy and entropy between the two reference states.

TABLE VI
PROPERTIES OF FLUID IN IDEALIZED OTTO-ENGINE PROCESS

State	p	T	E_s	E	H_s	H	S_s	S	v	$\frac{E+p_0v}{-T_0S}$
	lb/sq in. abs	F abs	Btu/lb of air				Btu/F lb of air		ft ³ /lb	Btu/lb of air
6'	14.7	550			44	1324	0.065	0.010		1319
1	14.7	640	24	1253	69	1298	0.1050	0.050	16.5	1272
2	157	1155	134	1363	214	1443	0.1050	0.050	2.75	1345
3	740	5010		1363		1739		0.5320	2.75	1094
4	90	3580		788		1063		0.5320	16.5	556
5-6	14.7	2500		470	661*	655*		0.5320	68	378
5''	14.7	3130				890		0.6135	87.5	432
6''	14.7	3010		613		840		0.598	83	529

* These two figures should be identical. There appears to be a slight inconsistency between enthalpies and internal energies in the chart for products.

TABLE VII
SECOND-LAW ANALYSIS OF AN IDEALIZED OTTO-ENGINE PROCESS

Event	Availability	Decrease in Availability	Useful Work	Irreversibility
	Btu/lb of air			
6 (with 6')	1281	9	0	9
1	1272	-73	-73	0
2	1345	251	0	251
3	1094	538	538	0
4	556	32	0	32
5 (with 5'')	524	1	0	1
6 (with 6'')	523			

The change in internal energy between the reference states is given on the H. E. & H. chart (for the unit of mass employed there) as $1280(1 - f)$, where f denotes the mass of unpurged products per unit mass of fluid. It is only necessary to add this quantity to the E_s or H_s of this chart in order to get the value of E or H relative to the reference state of the chart for the products.

The correction to the S_s of the air-fuel chart which will yield S on the same basis as the S of the chart for products is not given. It was necessary, therefore, to compute the value of this correction with the aid of the values for the change in H and F (our Z) given in the footnote on page 418 of the paper by H. E. & H. The computation yields an approximate value of 132 cal/kg mole for the difference between the entropy of the products and that of the air-fuel mixture at 1 atmosphere and 537 F abs. Adopting this value, we get the expression

$$S = S_s - 0.055$$

for the entropy of the air-fuel mixture unmixed with products of combustion. The entropy of a mixture of air and fuel with unpurged products was found by means of the Gibbs-Dalton Law for mixtures.

Table VII presents the Second Law analysis. It shows that the greatest irreversibility occurs in the process of combustion 2-3. The next greatest (though much smaller) occurs in the unrestrained expansion 4-5. A small degree of irreversibility results from mixing fresh charge with unpurged products in the process 6-1, and a still smaller from the mixing of exhaust gases in the process 5-6.

PROBLEMS

In the following problems assume the temperature of the medium (the atmosphere) to be 50 F (say 510 F abs) and its pressure to be 1 standard atmosphere.

The term *increase in availability* is used below in the general sense; that is, it may denote a quantity either greater or less than zero.

1. Find the availability of 1 lb of H_2O under a pressure of 100 lb/sq in. abs in the following conditions: (a) temperature = 1000 F, (b) saturated vapor, (c) saturated liquid, (d) temperature = 50 F, (e) temperature = 32 F.

2. Find the availability of 1 lb of H_2O at a temperature of 400 F in the following conditions: (a) pressure = 100 lb/sq in. abs, (b) saturated vapor, (c) saturated liquid, (d) pressure = 1000 lb/sq in. abs.

3. The availability is the maximum amount of useful work that could be obtained from the system in the presence of a stable atmosphere only. Describe a method by which this work could be realized for the state (a) of the preceding problem.

4. Plot a β - s chart for steam ($\beta = u + p_0 v - T_0 s$). Show: (a) the boundaries of the two-phase region, (b) the lines of constant pressure for pressures greater than and less than the critical pressure, (c) lines of constant temperature for temperatures greater than and less than the critical temperature, (d) the critical point, (e) the region of the triple point.

5. Find the increase in availability and the irreversibility corresponding to the following processes in each of which the system is 1 lb of H_2O which is initially at 200 lb/sq in. abs and 500 F.

(a) The system is confined at constant pressure by a piston and is heated until its volume is doubled.

(b) The same as (a) except that the change results from stirring instead of heating.

(c) The system expands reversibly and adiabatically behind a piston until its pressure is 100 lb/sq in. abs.

(d) It expands reversibly and isothermally behind a piston until its volume is doubled.

(e) It expands adiabatically into an adjacent chamber which is initially evacuated. The final pressure is 100 lb/sq in. abs.

(f) It is in motion with a total kinetic energy of 1 Btu/lb. Frictional effects cause it to come to rest. Assume no heat transfer and no change in pressure.

6. Show that the minimum amount of useful work that must be consumed to accomplish a process is equal to the increase in availability (in the absence of all reservoirs except the atmosphere). Show how the process (a) in the preceding problem might be accomplished by means of this minimum amount of work.

7. In each of the following processes a steady stream of H_2O enters an apparatus at low velocity and at 200 lb/sq in. abs and 500 F. Find for each process the increase in availability of each pound of H_2O as it passes through the apparatus, and the irreversibility.

(a) The stream is heated slowly at constant pressure until its temperature is 1000 F.

(b) It expands reversibly and adiabatically in a nozzle to 100 lb/sq in. abs.

(c) It expands reversibly and adiabatically to 100 lb/sq in. abs in a turbine which it leaves at low velocity.

(d) It expands adiabatically to 100 lb/sq in. abs through a porous plug which it leaves at low velocity.

(e) It expands isothermally to 100 lb/sq in. abs through a porous plug which it leaves at low velocity.

(f) It expands adiabatically to 100 lb/sq in. abs through a turbine of 60 per cent efficiency, leaving at low velocity.

(g) It is compressed reversibly and isothermally to 400 lb/sq in. abs.

8. Show how the decreases in availability which occur in processes (c), (d), (e), and (f) might be realized as useful work if the atmosphere is the only reservoir.

9. (a) One hundred Btu of heat is transferred slowly away from a constant-temperature reservoir which is at 150 F and which is exposed to a constant pressure of 1 standard atmosphere. Find the increase in availability and the irreversibility.

(b) The same as (a) except that -50 F is to be substituted for 150 F.

(c) One hundred Btu of heat is transferred slowly from the reservoir of (a) to that of (b). Find the increase in availability of the system comprising both reservoirs; and find the irreversibility of the process.

10. A gaseous system under a pressure of 1 atmosphere and having a constant specific heat at constant pressure of 3 Btu/degree F is used to supply heat for the evaporation of 1 lb of water from the saturated liquid state to the saturated vapor state at a pressure of 1 atmosphere. If the initial temperature of the gaseous system is 2000 F, find values of the increase in availability for the gas and for the water, and find the irreversibility of the process as a whole.

11. A steady stream of steam with a quality of 0.9 and at a temperature of 80 F is condensed in a condenser to saturated liquid at 80 F by means of a stream of cooling water which has a rate of flow which is 60 times the rate of flow of wet steam. The temperature of the cooling water is 50 F as it enters.

(a) Find the increase in availability of each pound of steam and each pound of cooling water.

(b) Find the irreversibility of the process experienced by the steam.

(c) Find the irreversibility of the process experienced by the cooling water.

(d) Find the irreversibility of the process as a whole per pound of steam.

(e) How do you account for the fact that the sum of (b) and (c) is not equal to (d)?

12. (a) Show that the effectiveness of a turbine of constant stage effectiveness is identical with the effectiveness of each stage.

(b) Derive [156], the statement that the effectiveness of a turbine is the weighted mean of the values of the effectiveness for its stages.

(c) Show that the condition curve of a turbine having uniform stage effectiveness is a straight line on the h - s chart and on the b - s chart.

13. Saturated steam at 50 lb/sq in. abs is fed to a mixing type of feed-water heater. Feed water is pumped from a condenser, which it leaves at a pressure of 1 in. Hg abs and in the saturated state, into the feed-water heater. The combined streams leave the heater as saturated liquid at 50 lb/sq in. abs. Assume the compression in the feed pump to be reversible and adiabatic.

(a) How much steam enters the heater for each pound of feed water entering?

(b) Find the increase in availability for each pound of liquid leaving the heater.

(c) Find the irreversibility of the process.

14. (a) A pound of O_2 at 1 atmosphere and 50 F is allowed to double its volume at constant temperature. Find the increase in availability.

(b) A pound of O_2 and a pound of N_2 each at 1 atmosphere and 50 F are allowed to mix adiabatically and without change in total volume. Find the increase in availability and the irreversibility.

(c) Find the minimum amount of work which would be necessary in order to restore the O_2 and N_2 to their respective initial states if no reservoir other than the atmosphere is employed.

15. A steady stream of air at 1 atmosphere, 50 F, and 20 per cent relative humidity is brought into contact with a stream of liquid water at 50 F. The two are allowed to come to equilibrium at constant temperature and at constant pressure.

(a) Find the amount and direction of the exchange of heat with other things.

(b) Find the increase in availability across the apparatus and the irreversibility of the entire process, both per pound of dry air entering.

(c) If this process were executed reversibly and the atmosphere was the only reservoir employed, how much useful work could be obtained?

16. (a) Compute values of the irreversibility for each of the processes in the reheat-regenerative process of Fig. 145.

(b) Compare the sum of the values of the irreversibility with the sum of the increases in availability for this cycle. How should these two sums be related in general?

17. Discuss the relative significance of the three properties, $\xi = h - T_s$, $\beta = u + p_0 v - T_0 s$, and $b = h - T_0 s$. In what respects are they similar as regards utility? Classify problems according to which property would be used in the solution. When do pairs of these properties become identical; and when are all three identical?

18. Employing the H. E. & H. charts and the information on the change in entropy resulting from combustion given on page 309, verify the data in Table VII for the idealized Otto-engine process.

SYMBOLS

b	$(h - T_0 s)$
e	internal energy of unit system in general
E	internal energy of system in general
E_s	internal energy reckoned from a special reference state
f	mass of unpurged products
g	acceleration given to unit mass by unit force
h	enthalpy per unit mass
H	enthalpy
p	pressure
Q	heat to system
s	entropy per unit mass
S	entropy
S_s	entropy reckoned from a special reference state
T	absolute temperature
u	internal energy of unit system in the absence of motion, gravity, etc
v	specific volume
V	volume
w	mass rate of flow
W	work
W_u	useful work
z	height

GREEK LETTERS

β	$(u + p_0 v - T_0 s)$
ϵ	effectiveness

η	efficiency
Δ	increase in property indicated
∇	decrease in property indicated

SUBSCRIPTS

e	expansion
p	pump
s	constant entropy, reference state

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CHAPTER XVIII

THE FLOW OF FLUIDS IN DUCTS

General Equations for Reversible Flow

In Chapter XI the dynamics and thermodynamics of a stream in steady flow are discussed from the standpoint of the designer of turbines. In the present chapter a somewhat broader view will be taken.

Let us consider a stream of fluid in steady flow which has at a section a (Fig. 148) uniform values of the velocity, V , the enthalpy, h , the height above some datum plane, z , and the pressure, p . It was shown on page 37 that the energy equation of steady flow [6] when applied to this section and a section b very near to it reduces to the equation

$$dh + d\left(\frac{V^2}{2g}\right) + dz - dQ = 0. \quad [6a]$$

It was also shown that the equivalent statement for *reversible* flow is Bernoulli's equation,

$$v dp + d\left(\frac{V^2}{2g}\right) + dz = 0,^* \quad [8]$$

which can be derived from Newton's Laws of Motion.

For the sake of simplicity we shall confine our discussion to those cases in which $dz = 0$, that is, those in which there is no appreciable change in level. When change in level and change in density are both appreciable the analytical results are interesting but of secondary im-

* The equivalence was proved above before the introduction of entropy. It may also be proved as follows:

For a pure substance in the absence of electricity, magnetism, and capillarity, we may write

$$T ds = du + p dv = dh - v dp. \quad [15]$$

For any reversible process

$$T ds = dQ.$$

Therefore

$$dQ = dh - v dp,$$

or

$$dh - dQ = v dp$$

for any reversible process. Substitution of $v dp$ for $dh - dQ$ in [6a] yields [8].

portance, except in meteorology. For the moment we shall concentrate our attention on the reversible case that is also adiabatic, since for that case we can trace the succession of states from the requirement of constant entropy.

Both [6a] and [8] may be applied in this instance, [6a] reducing to

$$dh + d\left(\frac{V^2}{2g}\right) = 0. \quad [6b]$$

and [8] to

$$v dp + d\left(\frac{V^2}{2g}\right) = 0. \quad [8b]$$

Consider two sections 1 and 2 which cross the stream a finite distance apart. Integration of [6b] and [8b] gives the equations

$$(h_2 - h_1) + \left(\frac{V_2^2}{2g} - \frac{V_1^2}{2g}\right) = 0 \quad [6c]$$

$$\int_1^2 v dp + \frac{V_2^2}{2g} - \frac{V_1^2}{2g} = 0 \quad [8c]$$

Which of these equations should be employed in any reversible adiabatic case depends upon the nature of the problem. In general, the quantity $(h_2 - h_1)$ may be evaluated by taking the difference between two quantities h_1 and h_2 selected from a table of properties. On the other hand, the evaluation of the integral of $v dp$ involves an integration which in turn demands a knowledge of all corresponding values of v and p between the limits of integration. Nevertheless, the second form of the equation is commonly used where the difference $(h_2 - h_1)$ is so small in view of the number of significant figures provided in the table that it cannot be determined directly with precision. Such cases normally occur where the change in pressure is small and where, therefore, the integral of $v dp$ can be determined readily by making a small correction to the quantity $v_1(p_2 - p_1)$.

A passage through which a stream flows without doing work on the boundary of the passage is called a *nozzle* if the pressure falls in the direction of flow, and a *diffuser* if the pressure rises in the direction of flow. For adiabatic flow in a nozzle or a diffuser [6b] and [6c] may be employed. For reversible adiabatic flow in a nozzle or a diffuser, [8b] and [8c] are equivalent forms of [6b] and [6c] respectively.

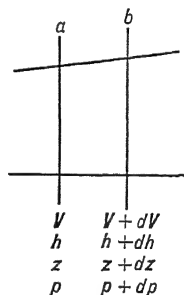


FIG. 148

The Incompressible Fluid and the Perfect Gas

Let us consider two cases for which the integral of $v dp$ can be expressed in terms of the properties at sections 1 and 2, namely, the case of an incompressible fluid and that of a perfect gas.

For an incompressible fluid we can obtain from [8c] an expression for the increase in kinetic energy between sections 1 and 2:

$$\frac{V_2^2 - V_1^2}{2g} = v(p_1 - p_2), \quad [157]$$

where v denotes the constant value of the specific volume of the fluid.

For a perfect gas the relation between p and v for an isentropic change of state is given by the equation

$$pv^k = \text{constant}, \quad [23]$$

where k is a constant which is equal to the ratio of the specific heats (see page 99). The integral in [8c] can therefore be readily evaluated, and the result may be expressed in the form

$$\frac{V_2^2 - V_1^2}{2g} = p_1 v_1 \frac{k}{k-1} \left[1 - \left(\frac{p_2}{p_1} \right)^{(k-1)/k} \right] \quad [158]$$

The condition of steady flow is one for which we may write

$$\frac{Va}{v} = w = \text{constant}.$$

If at any section 0 the cross-sectional area of the stream is very large then we have

$$V_0 = \frac{wv_0}{a_0} = 0.$$

Applying [6c] and [8c] to sections 0 and 1 and solving for the velocity at 1, we get

$$V_1 = \sqrt{2g(h_0 - h_1)} = \sqrt{2g \int_1^0 v dp}.$$

The flow through a unit of cross-sectional area at any section 1 is then given by

$$\left(\frac{w}{a} \right)_1 = \left(\frac{V}{v} \right)_1 = \frac{\sqrt{2g(h_0 - h_1)}}{v_1} = \frac{\sqrt{2g \int_1^0 v dp}}{v_1}$$

For an incompressible fluid this becomes

$$\left(\frac{w}{a}\right)_1 = \sqrt{\frac{2g(p_0 - p_1)}{v}}. \quad [159]$$

For a perfect gas it becomes

$$\left(\frac{w}{a}\right)_1 = \frac{1}{v_1} \sqrt{2gp_0v_0 \frac{k}{k-1} \left[1 - \left(\frac{p_1}{p_0}\right)^{(k-1)/k}\right]},$$

or in terms of v_0 (since $v_1 = v_0(p_0/p_1)^{1/k}$)

$$\left(\frac{w}{a}\right)_1 = \sqrt{2g \frac{p_0}{v_0} \frac{k}{k-1} \left(\frac{p_1}{p_0}\right)^{2/k} \left[1 - \left(\frac{p_1}{p_0}\right)^{(k-1)/k}\right]}. \quad [160]$$

Curves of Velocity and of Flow per Unit Area

The velocity of a real fluid may be obtained by means of [6c] and a table of properties. The flow per unit area is found upon dividing the

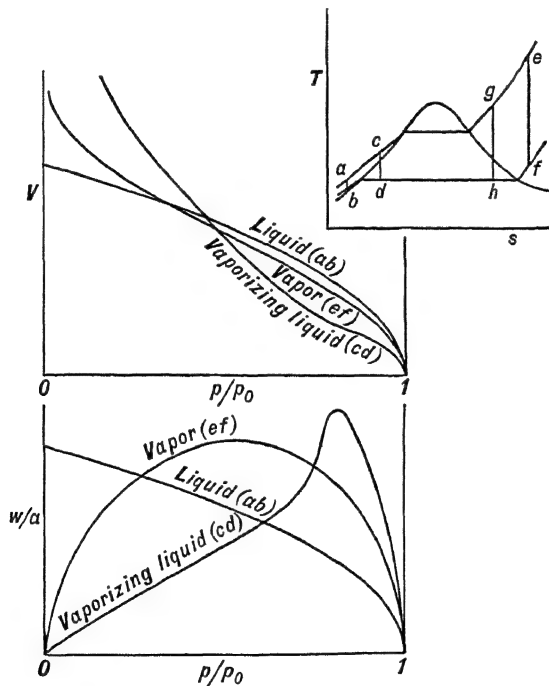


FIG. 149

velocity by the specific volume. In the temperature-entropy diagram of Fig. 149 are shown four types of reversible adiabatic expansion: expansion ab is entirely in the liquid phase, cd begins in the liquid

phase and ends in the two-phase region, ef is entirely in the vapor phase, and gh begins in the vapor phase and ends in the two-phase region.

In Fig. 149 are shown curves of velocity and flow per unit area for three of these types of expansion, namely, ab , cd , and ef . The curves for the fourth, gh , have characteristics so similar to those for ef that they are not shown separately. The curves calculated for an incompressible fluid by means of [157] are like those marked ab , and those calculated for a perfect gas by means of [159] and [160] are like those marked ef .

The Velocity of Sound

Both the vapor (ef) and the vaporizing liquid (cd)* exhibit maxima in the curve of flow per unit area. At the section corresponding to this maximum the cross-sectional area will be at a minimum. For the vapor it is easy to determine the velocity at this section: The derivative of the flow per unit area with respect to the velocity is

$$\frac{d(V/v)}{dV} = \frac{V}{v^2} \frac{dv}{dV},$$

which vanishes when

$$\frac{dV}{V} = - \frac{dv}{v}$$

This is the condition for which the flow per unit area is a maximum. From [8c] we get by differentiation

$$dV = - \frac{gv}{V} dp,$$

which when substituted into the previous equation yields the expression

$$- \frac{gv^2}{V^2} = \frac{dv}{dv} \quad [161]$$

or

$$\begin{aligned} V &= \sqrt{-gv^2 \frac{dp}{dv}} \\ &= \sqrt{k g p v}, \end{aligned} \quad [161a]$$

where k is defined by the equation

$$k = - \frac{v}{p} \left(\frac{\partial p}{\partial v} \right)_s = - \left[\frac{\partial (\ln p)}{\partial (\ln v)} \right]_s.$$

* Vaporization in the course of adiabatic flow is sometimes called cavitation.

That is, $(-k)$ is the slope of the isentropic at the state in question on a $\ln p$ - $\ln v$ diagram. (Of course, the isentropic need not be a straight line on this diagram; that is, it need not be of the form $pv^k = \text{constant}$.)

It was shown by Laplace* that the velocity of an infinitesimal sound wave (an infinitesimal disturbance) in a gaseous medium having pressure p and specific volume v is given by

$$\sqrt{k g p v},$$

which is identical with the expression for the velocity of a stream at the cross section of minimum area. That is, the velocity which a stream acquires in reversible adiabatic expansion at its cross section of minimum area is the same as the velocity of a sound wave through vapor that is similar in nature and in state to that in the cross section.

To show further that the two velocities are identical it is necessary first to recall that the expression for the velocity of sound is usually derived for a wave comprising an infinitesimal rise in pressure followed by an infinitesimal fall in pressure moving through a tube of constant cross-sectional area. It is assumed that the fluid is continuous and in a uniform state from wall to wall at any cross section at any instant (for the pressure is essentially uniform over any cross section and does not fall to zero at the tube wall when either part of the wave passes). Now if the observer were to move with the wave so that the wave would appear to him to be stationary, he would observe a stream of fluid flowing reversibly and adiabatically through a small rise in pressure and then through a small fall in pressure without any change in the cross-sectional area of the stream, or in its flow per unit area, of the same order of magnitude as the changes in pressure. Such behavior can be found only at a stream velocity corresponding to maximum flow per unit area, as will be seen from the curve marked *vapor* in Fig. 149. Therefore, the velocity of sound must be identical with the velocity of a stream at maximum flow per unit area.

The same reasoning will not apply to the case of vaporizing liquid where the maximum point in the curve of flow per unit area may be a cusp for which the rate of change of area with respect to pressure is not zero on either side of the maximum. The velocity of a sound wave in a two-phase medium depends upon relative motion of the two phases.

According to [161] the flow per unit area of an incompressible fluid never reaches a maximum. Therefore the velocity of sound in an incompressible fluid must be infinite. Since no pure liquid phase is in fact incompressible, the velocity of sound is in fact never infinite. It

* See Lamb, *Hydrodynamics*, p. 453.

is, however, very large, and it is the velocity that must be acquired by a stream if its flow per unit area is to reach a maximum.

The Throat of a Nozzle

Consider a converging-diverging nozzle to which a stream flows through a passage of very large cross-sectional area (section 0 of [160]). If a gas of known characteristics is supplied to this nozzle at a fixed pressure p_0 and a fixed specific volume v_0 the relation between flow per

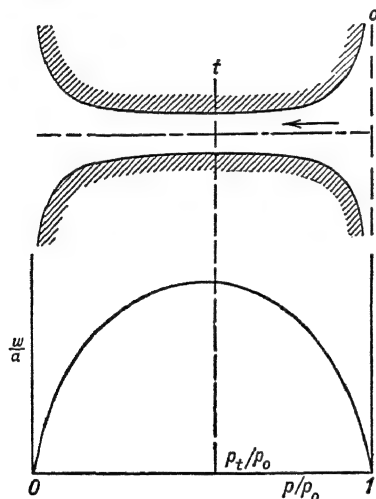


Fig. 150

unit area and pressure in the stream may be computed from [160] and plotted as in Fig. 150. The maximum flow that can pass through a unit area in any cross section of the passage is that given by the highest point on the curve of Fig. 150. Since this statement holds for the smallest section, or throat, of the nozzle, it follows that for maximum flow through the nozzle the pressure in the throat will be that, p_t , corresponding to the maximum flow per unit area. Moreover, this is the lowest pressure the stream can attain in the course of convergence. Any further decrease in pressure must be accompanied by divergence of the stream.

A curve showing the relation between flow per unit area and pressure (Fig. 150) may be used to determine the minimum pressure, p_t , that can exist in the throat of the nozzle. The curve may be based on values taken from a table of properties, or on an algebraic relation between properties in accordance with which the fluid expands. Thus, if a frictionless expansion occurs in accordance with the relation

$$pv^k = \text{constant},$$

as in a perfect gas, the ratio of the minimum pressure in the throat to the initial pressure can be found in terms of k by equating to zero the derivative of the flow per unit area [160] with respect to the pressure ratio. The result is

$$\frac{p_t}{p_0} = \left(\frac{2}{k+1} \right)^{k/(k-1)}.$$

Substituting this value in [158] and [160] we get an expression for the

velocity of sound,

$$V_s = \sqrt{2gp_0v_0 \frac{k}{k+1}} = \sqrt{kgp_v v_t}, \quad [162]$$

where v_t denotes the specific volume corresponding to p_t , and an expression for the maximum flow per unit area, $(w/a)_m$,

$$\left(\frac{w}{a}\right)_m = \sqrt{2g \frac{p_0}{v_0} \frac{k}{k+1} \left(\frac{2}{k+1}\right)^{2/(k-1)}} \quad [163]$$

When the pressure in the chamber into which a nozzle discharges (which we shall call the exhaust pressure) is lowered to the point where the pressure in the throat of the nozzle is at its minimum value, a further decrease in the exhaust pressure will not alter the pressure in the throat. Indeed, for all lower values of the exhaust pressure the velocity and properties of the fluid in the throat will remain unchanged. Moreover, the flow will remain unchanged because no change can occur in velocity or specific volume in the throat.

At sections downstream from the throat the pressure may be less than the throat pressure and the velocity may exceed the velocity of sound. Under these conditions no sound or other disturbance of the fluid which originates in the exhaust chamber could ever pass up the stream into the inlet chamber of the nozzle. Osborne Reynolds used this concept to explain why the flow through a nozzle reaches a maximum value which is maintained for all further decrease in the pressure in the exhaust chamber. He pointed out that a decrease in pressure would fail to travel upstream to the throat of the nozzle, and, therefore, the fluid in the throat would be "unaware" of the change in conditions in the exhaust chamber. Conditions in the throat would thus remain unchanged.*

A steady flow of vaporizing liquid will pass through a *throat* in the course of expansion as indicated by its curve of flow per unit area, but the velocity in the throat will not be the velocity of sound. No throat appears in an expanding stream of incompressible fluid.

Since the cases discussed above are, by assumption, reversible, the discussion applies equally well to a diffusing stream as to an expanding stream. It should be noted that where the slope of the curve of flow per unit area with pressure is negative (Fig. 150) a nozzle is a converging passage and a diffuser is a diverging passage in the direction of flow; when the slope is positive the reverse is true.

* This explanation is of limited utility. It fails to show, for example, why a converging-diverging nozzle will have within it velocities in excess of the velocity of sound when the velocities at entrance and exit are well below that of sound.

Work in Reversible Steady-Flow Processes

When work is delivered to things outside a steady-flow system we may find the magnitude of the work, W_x , from [6]:

$$W_x = h_1 - h_2 + \frac{V_1^2}{2g} - \frac{V_2^2}{2g} + z_1 - z_2 + Q. \quad [164]$$

If the flow through the apparatus in question is reversible we may substitute $T ds$ for dQ and the work delivered becomes

$$W_x = h_1 - h_2 + \frac{V_1^2}{2g} - \frac{V_2^2}{2g} + z_1 - z_2 + \int_1^2 T ds;$$

or, since

$$dQ_{\text{rev.}} = T ds = dh - v dp,$$

$$W_x = \int_2^1 v dp + \frac{V_1^2}{2g} - \frac{V_2^2}{2g} + z_1 - z_2. * \quad [165]$$

Equations [164] and [165] are used in the solution of problems in reversible flow through engines, turbines, compressors, and similar devices.

Irreversible Flow (Flow with Friction) in a Stream Tube

When a stream experiences wall friction or other irreversible phenomena we may still apply the energy equation of steady flow in its general form [6] to any two sections along the path of the stream. Equation [6], however, is no longer identical with the dynamic equation [8]; nor

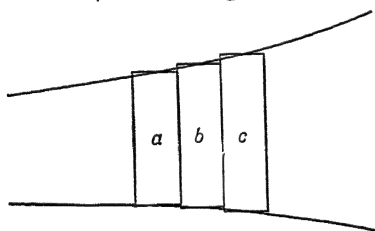


FIG. 151

should it be, since the First Law of Thermodynamics and Newton's Laws of Motion, from which the two are respectively derived, are not equivalent.

In irreversible flow the velocity in any cross section of a stream may be non-uniform in direction and magnitude. Therefore, it is best for analytical purposes to consider an element of fluid small in all dimensions. For simplicity, let us divorce the problem from the gravitational field.

* The restriction to reversibility in [165] must never be ignored. The absurdity of the application of [165] to an irreversible case is made evident by the Joule-Thomson experiment for which it reduces to

$$\int v dp = 0,$$

despite the fact that the p - v relation for this case commonly approximates

$$pv = \text{constant}.$$

Consider an element of fluid which at some instant occupies the volume a , Fig. 151, and a moment later occupies an adjacent space b . The right-hand boundary of a and the left-hand boundary of b will coincide except for distances of a smaller order than the thickness of a , provided that the velocity does not vary discontinuously at any point. The fluid originally occupying space b will occupy an adjacent space c when fluid from the first element has moved to space b . By similar reasoning we may trace out a continuous series of elementary volumes, a, b, c , etc., which together constitute a *stream tube*.*

In Chapter XI (page 150) a dynamic analysis is made of flow in a stream tube, and the result is the vector equation

$$\mathbf{F} + (\mathbf{p}a)_1 - (\mathbf{p}a)_2 + (\mathbf{S}a)_1 - (\mathbf{S}a)_2 = \frac{w}{g}(\mathbf{V}_2 - \mathbf{V}_1); \quad [58]$$

where subscripts 1 and 2 refer to sections a finite distance apart, \mathbf{F} denotes the vector representing the force which is applied to the portion of the stream tube between those two sections by fluid outside its boundaries, $\mathbf{p}a$ a vector representing the normal force applied at a section by fluid upstream from that section, $\mathbf{S}a$ a vector representing the shearing force applied at a section by fluid upstream from that section, \mathbf{V} a vector representing the velocity at a section, w the mass rate of flow, and g the acceleration given to unit mass by unit force.

Friction in a Finite Stream

It must be remembered that the analysis just referred to was applied to a stream tube of such small dimensions that the velocity is uniform in each cross section, and, therefore, w , \mathbf{F} , $\mathbf{p}a$, and $\mathbf{S}a$ are infinitesimal in magnitude. We may extend the analysis to cover finite streams as follows: Consider a stream tube d , Fig. 152, surrounded by the annular tube e , which is in turn surrounded by annular tube f , etc. Now let \mathbf{F}_d denote the vector which represents the force applied to the fluid in tube d , at the boundary between tubes d and e , \mathbf{F}_e the vector which represents the force applied to the fluid in tube e at the boundaries between tube e and adjacent tubes, etc. The force \mathbf{F}_d which is applied to stream d is

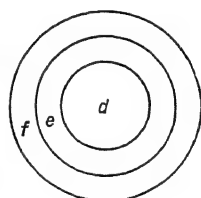


FIG. 152

* Glauert, in *Aerofoil and Airscrew Theory* (Cambridge, 1930), p. 10, defines a stream tube as a cylindrical surface formed by the stream lines which pass through a closed curve, and a stream line he defines in turn by the condition that its direction at any point is the direction of motion of the fluid element at that point. This definition and that given above are identical. It should be noticed that neither implies that a fluid element in a given stream tube at one section of the stream will at a later time be in the same stream tube at another section a finite distance away.

applied solely by the fluid of stream e , so that stream d applies to stream e a force $-\mathbf{F}_d$. But the net force applied to tube e is \mathbf{F}_e . Therefore the force \mathbf{F}' applied to stream e at its outside boundary can be found from the equation

$$\mathbf{F}_e = \mathbf{F}' - \mathbf{F}_d,$$

or

$$\mathbf{F}' = \mathbf{F}_d + \mathbf{F}_e.$$

Similarly it can be shown that the force \mathbf{F}'' applied to the outside boundary of tube f is given by

$$\mathbf{F}'' = \mathbf{F}_d + \mathbf{F}_e + \mathbf{F}_f,$$

and, in general, the force applied by any boundary surrounding any finite stream is

$$\int d\mathbf{F},$$

where $\int d\mathbf{F}$ denotes the summation of all the net boundary forces which are applied to elementary stream tubes.

We may apply [58] to a finite stream by summing up the values of each term for all the elementary stream tubes that constitute the finite stream. The summation for the term \mathbf{F} will be, in view of the argument just presented, the vector representing the force applied to the stream by the boundaries of the stream between sections 1 and 2. The sum of each term $\mathbf{p}a$ will be a vector which is the resultant of all the elementary vectors corresponding to the normal forces at the section. The sum of each term $\mathbf{S}a$ will have a similar significance with respect to shearing forces at the section. The sum of each term $(w/g)\mathbf{V}$ will be a vector representing the flow of momentum per unit time across the section.

Letting \mathbf{F}_{12} , \mathbf{P} , \mathbf{S} , and \mathbf{M} denote the summations in the order given above, we get

$$\mathbf{F}_{12} + \mathbf{P}_1 - \mathbf{P}_2 + \mathbf{S}_1 - \mathbf{S}_2 = \mathbf{M}_2 - \mathbf{M}_1. \quad [166]$$

If the boundaries of the finite stream are at rest (at least, relative to each other) then each summation \mathbf{S} across a section is generally small compared with the other terms in [166], because the velocity gradients (and hence the shear forces) must be both positive and negative in any direction in the same section. Therefore, [166] may be simplified to

$$\mathbf{F}_{12} + \mathbf{P}_1 - \mathbf{P}_2 = \mathbf{M}_2 - \mathbf{M}_1. \quad [167]$$

Using the subscript x to denote a component of the corresponding vector

in one direction, we may take [166] out of the vector form; thus,

$$F_x + P_{1x} - P_{2x} = M_{2x} - M_{1x}. \quad [168]$$

Then F_x is the component in the x direction of the force applied to the stream by the wall, and $-F_x$ is the component in the x direction of the reaction of the stream on the wall.

We may find the magnitude of P_x by integrating over the entire sectional area the expression

$$p \cos \alpha \, da,$$

where p denotes the pressure over the elementary sectional area da , and α the angle between a normal to the plane of that area and the direction of x (Fig. 153). We may find the magnitude of M_x by integrating over the cross-sectional area the expression

$$\frac{G}{g} V \cos \alpha \, da,$$

where G denotes the mass flow per unit area at the elementary area da , and V the resultant velocity there. An equivalent expression is

$$\frac{G}{g} V_x \, da,$$

where V_x denotes the component of the velocity in the x direction.

Equation [168] is useful in determining the net force in the direction of flow applied by a stream to the walls enclosing it. In combination with equations of energy and continuity it will solve many problems. To get the force required to hold a duct in position it is necessary to know the force applied from outside as well as that applied from inside by the stream, but the outside force is often mere static pressure and can be easily calculated.

The Coefficient of Friction

It is known from experience that the flow of a viscous fluid may be of one of two types: namely, laminar flow, in which each element of fluid remains within a single stream tube (page 323) in the course of its flow, and turbulent flow, in which the element may leave the stream tube. In laminar flow in a transparent tube a colored filament introduced into the stream will remain a separate filament easily distinguishable from

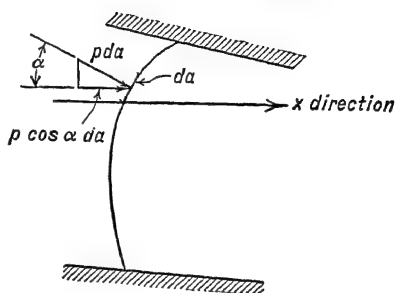


FIG. 153

the remainder of the fluid throughout the length of the stream. In turbulent flow the colored filament is quickly dispersed throughout the stream until it is no longer distinguishable as a separate part of it. The friction applied to a wall by a stream varies in a characteristic manner for each of these two types of flow.

Let us define a coefficient of friction f by the equation

$$f = \frac{R}{\rho V^2} \quad [169]$$

where R denotes the frictional force applied to a unit area of wall surface, ρ the mass density of the fluid, and V its mean resultant velocity. It can be shown by dimensional reasoning* that for geometrically similar passages this coefficient is some function of two dimensionless products; thus

$$f = f\left(\frac{V d \rho}{\mu}, \frac{V}{V_s}\right), \quad [170]$$

where d denotes a dimension of the passage, μ the coefficient of viscosity of the fluid, and V_s the velocity of sound in the fluid. The products $V d \rho / \mu$ and V / V_s are known respectively as the Reynolds number and the Mach number.

It has been shown by analysis and by experiment† that in laminar flow the coefficient of friction varies inversely as the Reynolds number

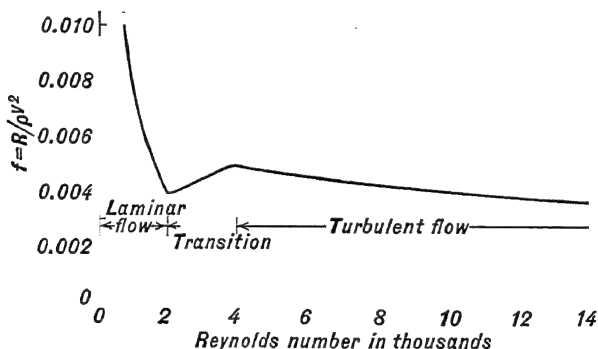


FIG. 154. Friction Coefficients for Laminar and Turbulent Flow in Smooth Pipes

(Fig. 154) as long as the Mach number is near zero, which is almost always true since laminar flow occurs only at low Reynolds numbers and hence, with rare exception, at low velocities. For turbulent flow in smooth

* *Fluid Mechanics for Hydraulic Engineers*, Rouse, McGraw-Hill, 1938, p. 23.

† *Ibid.* p. 246.

pipes the coefficient of friction decreases slowly with increase in Reynolds number (Fig. 154).^{*} Recent experiments[†] indicate that in turbulent flow the value of f is almost independent of the Mach number, so that we may write

$$f = f\left(\frac{Vd\rho}{\mu}\right) \quad [171]$$

for turbulent flow even when the density is variable.

Equations for Flow with Friction

Measured values of the coefficient of friction can be used to determine the characteristics of the flow of a fluid through a passage of given dimensions. For steady flow in general we may write as conditions which must be fulfilled by a stream in each step of its progress the energy equation

$$dh + \frac{V dV}{g} - dQ = 0 \quad [172]$$

(which may be obtained from [6a] by ignoring change in elevation), the continuity equation

$$d\left(\frac{Va}{v}\right) = 0 \quad [173]$$

(which may be obtained from [9]), and the dynamic equation

$$d(pa) + \frac{w}{g} dV - dF = 0 \quad [174]$$

(which may be obtained from [168]).[‡]

Into the last equation the coefficient of friction f may be introduced by expressing the wall force in terms of it. Consider an element of wall surface which exerts on the fluid the force component dF in the direction of the velocity V . Part of this force component is a reaction to the normal pressure of the fluid on the wall.

Consider a piece of a passage which is bounded by two cross sections which are normal to the direction of flow and which are separated by

^{*} For more complete data see Bakhmeteff, *The Mechanics of Turbulent Flow*, Princeton University Press, 1936, Fig. 24.

[†] Frössel, *Forschung a.d. Gebiete d. Ingenieurwesens*, Vol. 7 (1936), pp. 75-84. Egli, *Trans. A.S.M.E.*, Vol. 59 (1937), p. A-63. Keenan, *Trans. A.S.M.E.*, Vol. 61 (1939), pp. A-11 to A-20.

[‡] Each of these equations is expressed for simplicity in terms of mean values of the variables; for example, if we let l denote distance in direction of flow, $dh = \frac{d}{dl}\left(\frac{\int h dw}{w}\right)dl$, and $\frac{w}{g} dV = \frac{d}{dl}\left(\frac{1}{g} \int V dw\right)dl$, the integrals being evaluated over the entire flow through the cross-sectional area. The more exact expressions may be substituted at any stage in the analysis.

the infinitesimal distance dl (Fig. 155). The wall surface of this piece of the passage may be thought of as consisting of narrow strips extending between the two cross sections. Let dl' denote the length of one of these strips, and let δy denote its other dimension. Then the resultant normal force on this strip has a magnitude which lies between

$$p \, dl' \, \delta y \quad \text{and} \quad (p + dp) \, dl' \, \delta y,$$

where p denotes the pressure at the upstream section and $p + dp$ that at the downstream section. Since these two values of the normal force differ by a quantity of an order smaller than either, we may express the normal force by $p \, dl' \, \delta y$. The direction of this force makes an angle α with the direction of flow, and the component of this force in the direction of flow is, therefore,

$$p \, dl' \, \delta y \cos \alpha.$$

Now $dl' \, \delta y \cos \alpha$ is the projection of the piece of wall surface of magnitude $dl' \, \delta y$ on the downstream cross section. The component of the normal

force is, therefore, $p \, \delta a$, where δa denotes the area of the projection. Summing up the components of the normal forces for all the strips of wall surface, we get for the total component of the normal forces,

$$p \, da,$$

where da denotes the amount that the cross-sectional area of the downstream section exceeds that of the upstream section.

The remainder of the force component dF is a component, in the direction of flow, of the shear force at the wall. For the elementary strip of wall surface this component is given by

$$-R \, \delta y \, dl' \sin \alpha = -R \, \delta y \, dl,$$

where R denotes the frictional force per unit area of wall surface. Summing up for all the strips of wall surface, we get for the total component of the shear forces

$$-Ry \, dl,$$

where y denotes the perimeter of the passage.

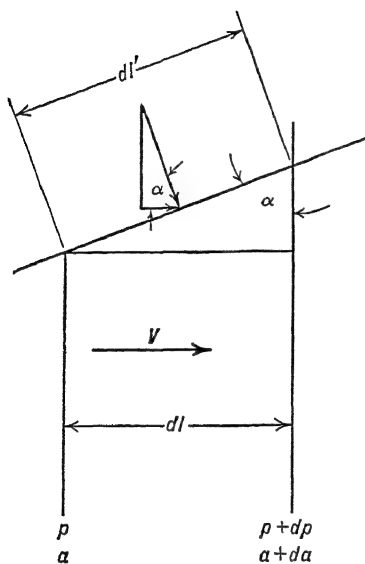


FIG. 155

Combining the two parts we get

$$dF = p da - Ry dl.$$

Upon substitution for dF the dynamic equation [174] becomes

$$d(pa) - p da + \frac{w}{g} dV + Ry dl = 0,$$

or

$$a dp + \frac{w}{g} dV + Ry dl = 0. \quad [175]$$

Since $R = \ell \rho V^2$, [174] is also given by

$$a dp + \frac{w}{g} dV + \ell \rho V^2 y dl = 0, \quad [176]$$

which, when multiplied through by v/a , becomes

$$v dp + \frac{V}{g} dV + \ell \frac{V^2}{ga} y dl = 0.* \quad [177]$$

* In discussions of the flow of fluids in pipes an equation of the form

$$v dp + \frac{V}{g} dV + dL = 0 \quad [a]$$

is often found. It is usually stated that dL is the "loss of energy due to friction." Since no energy passes from fluid to wall as a result of friction the meaning of the phrase is not clear. By comparison of [a] with the general energy equation [6a] reduced to the adiabatic case, namely,

$$dh + \frac{V}{g} dV = 0,$$

we find that dL in the above equation is given by

$$dL = dh - v dp \quad [b]$$

$$= du + p dv \quad [c]$$

$$= T ds. \quad [d]$$

Equation [c] indicates that dL is analogous to the transfer of energy to a system at rest. That is, if the observer moves with the fluid element, dL is the work he observes to be done on it by adjacent walls (or adjacent fluid) which move relative to it. In this sense it is a gain in energy. Equation [d] reminds one of a common confusion of $T ds$ in an irreversible process with heat, or, as in this case, with a transfer of energy.

By comparing [a] with [177] dL can be expressed in terms of the friction force or the friction coefficient:

$$dL = \ell \frac{V^2}{ga} y dl.$$

It is best to think of friction always in terms of force and never in terms of energy. It is true that, when the force moves as it is applied to a system, energy is transferred to the system, but in the case of the fluid stream the friction force is usually applied by a stationary wall so that no energy is transferred.

Using the continuity equation in the forms

$$V = \frac{wv}{a}$$

and

$$dV = w \left(\frac{dv}{a} - \frac{v da}{a^2} \right)$$

we may eliminate the velocity. Equation [177] then becomes

$$v dp + \frac{w^2}{g} \left(\frac{v}{a^2} dv - \frac{v^2}{a^3} da + \frac{\ell}{g} w^2 \frac{v^2 y}{a^3} dl \right) = 0. \quad [178]$$

Flow through a Pipe

As an example of the application of [178] consider the flow of a fluid through a pipe of constant cross-sectional area. Since for each step in the path of flow $da = 0$, [178] reduces to

$$v dp + \frac{1}{g} \left(\frac{w}{a} \right)^2 v dv + \frac{w^2 y}{ga^3} \ell v^2 dl = 0, \quad [179]$$

or, after being divided through by v^2 , to

$$\frac{dp}{v} + \frac{1}{g} \left(\frac{w}{a} \right)^2 \frac{dv}{v} + \frac{w^2 y}{ga^3} \ell dl = 0. \quad [180]$$

Along the length of a pipe of constant cross-sectional area the Reynolds number, which can be expressed as

$$\frac{wd}{g\mu},$$

varies inversely as μ . Frequently the change in μ along the pipe is small and the change in ℓ is relatively much smaller. Therefore we may assume ℓ to have a constant value which is in reality a mean between its end values. Integrating between two sections 1 and 2 which are a finite distance apart we get

$$\int_1 \frac{dp}{v} + \frac{1}{g} \left(\frac{w}{a} \right)^2 \ln \frac{v_2}{v_1} + \frac{w^2 y}{ga^3} \ell l = 0, \quad [181]$$

where l denotes the distance between the two sections.

The magnitude of the first term in [181] depends directly, and that of the second term indirectly, on the relation between pressure and volume along the path of flow. To get this relation we assume adiabatic conditions and write the energy equation [172] in the form

$$h + \frac{V^2}{2g} = h_0,$$

where h_0 is a constant, and the continuity equation [173] in the form

$$V = \frac{w}{a} v.$$

Substituting the latter in the energy equation we get

$$h + \left(\frac{w}{a}\right)^2 \frac{v^2}{2g} = h_0,$$

or

$$h + \left(\frac{w}{a}\right)^2 \frac{v^2}{2g} = h_1 + \left(\frac{w}{a}\right)^2 \frac{v_1^2}{2g}, \quad [182]$$

where subscript 1 denotes a property of the fluid at any specified section across the stream. The relation between h and v given by [182] is in reality an infinite number of relations each corresponding to a different value of w/a and each passing through the state corresponding to h_1 and v_1 . Figure 156 shows a series of lines representing [182] on an h - s diagram for a state 1. They are called *Fanno lines*.*

Interpretation of the Fanno Lines

The isenthalpic through state 1 is the Fanno line for zero (negligible) flow. For some higher flow the curve sweeps to higher entropies as the enthalpy decreases. At some pressure the entropy reaches a maximum (m , Fig. 156); and it decreases with any change in pressure. Since an adiabatic change to lower entropy would contravene the Second Law (see page 88) an expansion at constant area cannot proceed

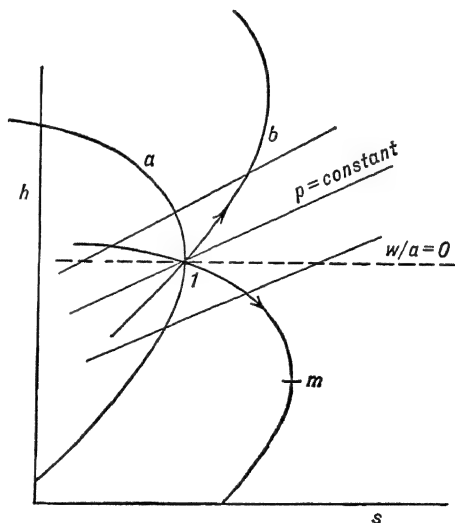


FIG. 156. Fanno Lines

beyond m . If the pressure in the chamber into which the pipe exhausts is lower than the pressure at m , then the fall in pressure from m to the exhaust pressure must occur outside the pipe where the stream is not restricted to constant area. Any small change of state along the curve at

* *Steam and Gas Turbines*, Stodola-Lowenstein, McGraw-Hill, 1927, Vol. 1, p. 61.

the point of maximum entropy is a change at constant entropy; therefore, we may write

$$T ds = 0 = dh - v dp.$$

From the Fanno-line equation, we get

$$dh + \frac{1}{g} \left(\frac{w}{a} \right)^2 v dv = 0.$$

Equating and solving for dv/dp we get

$$\frac{dv}{dp} = -g \frac{v^2}{V^2}, \quad [161]$$

which according to [161a] is the condition for which the velocity of the fluid is the velocity of sound:

$$V = V_s.$$

The part of the curve below m has practical significance, though it cannot be approached through state m . When the flow in the pipe is large enough to produce the velocity of sound at state 1 the Fanno line is the one (labeled a) with infinite slope at 1. For higher flows, that is, for velocities in excess of the velocity of sound, the Fanno line has a positive slope at 1 and the flow corresponds to conditions below point m (as for state 1 on curve b). As the fluid moves down the pipe its entropy increases and, therefore, its pressure increases. Thus friction in a pipe may cause either a fall in pressure or a rise in pressure, depending upon whether the velocity is less than or greater than the velocity of sound.

Measuring the Coefficient of Friction

Consider a pipe of constant cross-sectional area with a well-rounded inlet (Fig. 157) toward which a fluid flows at negligible velocity in state 0. For sections 1 and 2 across the pipe we may write [182] in the form

$$h_1 + \left(\frac{w}{a} \right)^2 \frac{v_1^2}{2g} = h_2 + \left(\frac{w}{a} \right)^2 \frac{v_2^2}{2g} = h_0,$$

and [181]

$$\int_1^2 \frac{dp}{v} + \frac{1}{g} \left(\frac{w}{a} \right)^2 \ln \frac{v_2}{v_1} + \frac{w^2 y}{ga^3} fl = 0. \quad [181]$$

The value of w/a may be measured or it may be assumed to be that corresponding to reversible, adiabatic flow between sections 0 and 1 (page

136). In either case the Fanno line may be plotted in accordance with [182]. The pressure-volume relation, as determined by the equation of the Fanno line and the tabulated properties of the fluid, permits a graphic evaluation of the first term of [181]. The same relation will provide volumes corresponding to p_1 and p_2 for the second term. If the pressures at 1 and 2 are measured the value of f can be found from [181].

An algebraic method that will be suitable for vapors, as a rule, depends on the assumption that the equation

$$h = A + Bpv, \quad [183]$$

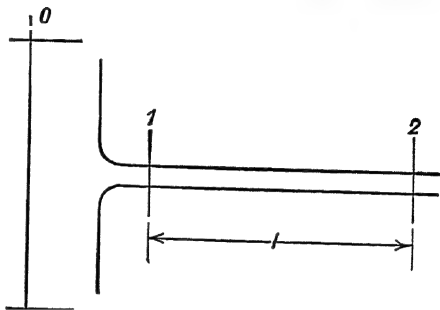


FIG. 157

where A and B are constants, satisfactorily represents the h - p - v relation. Substituting this into the equation for the Fanno line [182], we get

$$A + Bpv + \left(\frac{w}{a}\right)^2 \frac{v_2^2}{2g} = h_0,$$

or

$$\alpha v^2 + Bpv + c = 0,$$

where

$$\alpha = \frac{(w/a)^2}{2g} \quad \text{and} \quad c = A - h_0.$$

Then at any pressure the specific volume is given by

$$v = \frac{-Bp \pm \sqrt{B^2 p^2 - 4\alpha c}}{2\alpha} \quad [184]$$

The first term of [181] is now

$$\int_{v_1}^{v_2} \frac{dp}{v} = -\frac{\alpha}{B} \ln \frac{v_2}{v_1} + \frac{1}{2} \frac{c}{B} \left(\frac{1}{v_2^2} - \frac{1}{v_1^2} \right).$$

The coefficient of friction corresponding to measured values of the pressure at 1 and 2 can be found by substituting into [181] the values of the volumes from [184]. By this method and related methods the values of the coefficient of friction shown in Fig. 158 for the flow of compressible fluids were computed from measurements of pressure and flow.

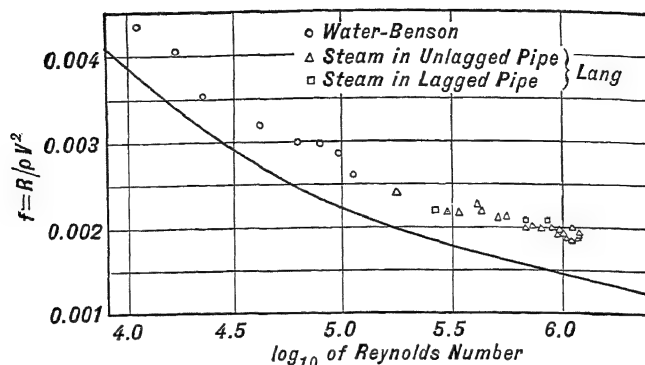


FIG. 158. The Coefficient of Friction for Commercial 1-Inch Pipe

The solid line represents Nickuradse's equation for incompressible fluids in smooth pipes. From Keenan, *Trans. A.S.M.E.*, Vol. 61 (1939), pp. A-11-A-20.

Pressure Shock and the Rayleigh Line

It is known that a stream flowing at a velocity greater than the velocity of sound will often establish a standing wave of compression through

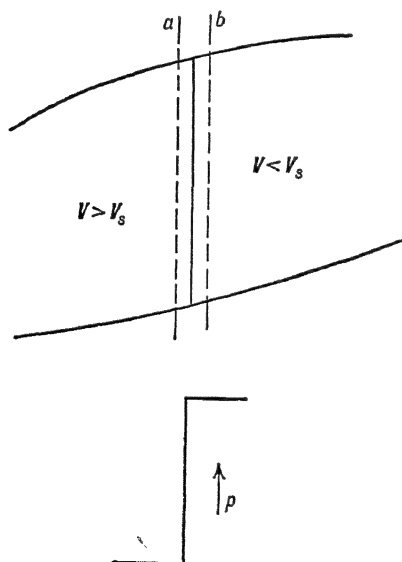


FIG. 159

which the fluid flows, and from which it leaves at a velocity less than the velocity of sound (Fig. 159). It would seem that the action is inherently irreversible in that a standing wave of rarefaction is never established. This observation is verified analytically in the following paragraphs.

If the standing wave may be considered to be of infinitesimal depth in the direction of stream flow, then the cross-sectional area of the stream does not change as it flows through the wave. Since this restriction and the energy requirements are comprised within the equation for the Fanno line, the state of the fluid on either side of the wave must lie on the same Fanno line.

The dynamic equation [168] when applied to sections a and b on either side of the wave (Fig. 159) reduces to

$$\frac{w}{g} (V_b - V_a) + (p_b - p_a)a = 0, \quad [185]$$

since no wall forces of finite magnitude are applied to the stream between a and b . Eliminating velocities from [185] through the continuity equation [173] and solving for p_b , we get

$$p_b = p_a - \frac{1}{g} \left(\frac{w}{a} \right)^2 (v_b - v_a). \quad [186]$$

This is the equation of a Rayleigh line,* which is the locus of a point representing the state that could be assumed by fluid which passes through state a in steady flow provided that it is subjected to no external force between section a and the section corresponding to the new state. In order that the fluid might assume one of these states it would in general be necessary that heat should flow to or from it. There is, however, one state to which the fluid could change with a heat flow of zero: that is, the state (b , Fig. 160) corresponding to the intersection of the Rayleigh line with the Fanno line.

The equations of the Fanno line and the Rayleigh line are, respectively, statements of the conditions imposed by the First Law and the Laws of Motion. Thus, these conditions would not be violated if fluid in state a were to change suddenly and spontaneously to a state b ; nor would they be violated if the reverse change (from b to a) were to occur.

However, of these two states the one at higher enthalpy (b , Fig. 160) is also at higher entropy; and, since the process is adiabatic, a change from the one at higher entropy to the other would contravene the Second Law. Therefore the change will be to higher entropy, enthalpy, and pressure, and the wave is a wave of compression. Moreover, since the enthalpy at b is higher than that at m , where the velocity is the velocity of sound, the velocity at b is less than the velocity of sound. A stream can enter a shock only if it is moving at a velocity greater than that of sound (corresponding to a , Fig. 160); it will issue from the shock at a velocity less than that of sound (corresponding to b , Fig. 160).

If it is permissible to represent the h - p - v relation by the equation

$$h = A + Bpv, \quad [183]$$

we can devise an algebraic solution for the state b of the fluid issuing from

* *Steam and Gas Turbines*, Stodola-Lowenstein, McGraw-Hill, 1927, Vol. 1, p. 86.

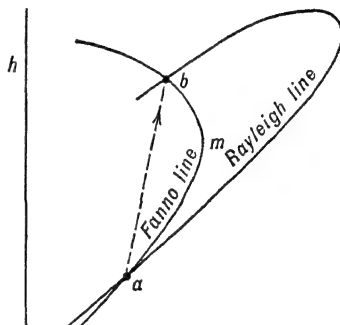


FIG. 160

a shock in terms of the state a of the fluid entering the shock and the flow per unit of cross-sectional area, w/a .

Combining [183] with the equation of the Fanno line

$$h_b + \left(\frac{w}{a}\right)^2 \frac{v_b^2}{2g} = h_0$$

and the equation of the Rayleigh line

$$p_b = p_a - \frac{1}{g} \left(\frac{w}{a}\right)^2 (v_b - v_a),$$

we get the quadratic

$$\left(\frac{w}{a}\right)^2 \left(\frac{1}{2g} - \frac{B}{g}\right) v_b^2 + \left[Bp_a + \frac{1}{g} \left(\frac{w}{a}\right)^2 v_a\right] v_b + (A - h_0) = 0,$$

which may be solved for v_b . The value of v_b when substituted in the two equations preceding the last determines the values of p_b and h_b .

PROBLEMS

1. From the *Steam Tables* plot $(h - h_0)$ against pressure for pressures from 10 to 1000 lb/sq in. abs for the isentropic passing through the state $p_0 = 100$ lb/sq in. abs, $t_0 = 600$ F.

By means of a graphic or approximate numerical method of integration calculate

$\int_{p_0}^p v dp$ over the same range and in the same units and plot on the same diagram.

Plot the approximation to the integral, $v_0(p - p_0)$, in the same way.

2. In the following problems plot against the ratio of the pressure in the stream to the pressure before the nozzle, where the velocity is negligible, values of temperature, specific volume, kinetic energy per unit mass, velocity, and flow per unit area for reversible adiabatic flow. The subscript 0 refers to the *inlet* section, where the velocity is negligible.

$p_0 = 20$ lb/sq in. abs, $T_0 = 700$ F, expansion of H_2O .

$p_0 = 20$ lb/sq in. abs, $v = 34.47$ ft³/lb, incompressible flow.

$p_0 = 20$ lb/sq in. abs, $v_0 = 34.47$ ft³/lb, expansion in accordance with the relation $pv^{1.31} = \text{constant}$.

$p_0 = 400$ lb/sq in. abs, $t_0 = 400$ F, expansion of H_2O .

3. Derive expressions for specific volume, kinetic energy, velocity, and flow per unit area corresponding to an expansion for which $pv^k = \text{constant}$. Express these quantities for the section at which the pressure is p in terms of p_0 , v_0 , and p/p_0 .

If the gas is a perfect gas, state the same equations in terms of p_0 , T_0 , and p/p_0 .

From the expression for flow per unit area derive the expression

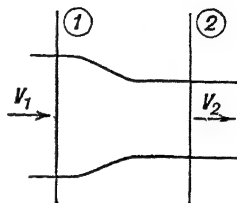
$$\frac{p_t}{p_0} = \left(\frac{2}{k+1}\right)^{k/(k-1)}$$

for the pressure ratio corresponding to the throat of a converging-diverging nozzle.

4. A stream of fluid in steady flow enters a passage at velocity V_1 which is uniform over the entire cross-sectional area a_1 of the stream. It leaves at a velocity V_2 which is uniform over the entire cross-sectional area a_2 of the stream.

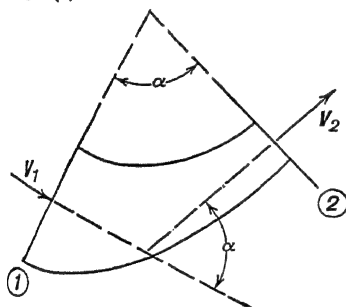
(a) Derive an expression for the force applied by the walls of the passage to the stream between sections 1 and 2 in terms of areas, velocities, pressures, and mass rate of flow at the two sections.

(b) Assume that this passage extends only between sections 1 and 2, and that all surfaces of the passage wall which are not in contact with the stream are exposed to a pressure p_2 which is identical with that at section 2. Find the magnitude and direction of the force necessary to hold the passage walls in place.



(c) If $p_1 = 100$ lb/sq in. abs, $t_1 = 600$ F, $V_1 = 100$ ft/sec, $p_2 = 60$ lb/sq in. abs, $a_2 = 1$ sq ft, the fluid is steam, and the process between 1 and 2 is reversible and adiabatic, find the magnitude of the force applied by the walls of the passage to the stream and of the force necessary to hold the passage walls in place.

5. (a) If the sections 1 and 2 are not parallel and the velocities are normal to their corresponding sections and are directed at an angle α to each other, derive expressions for components of the force applied by the wall to the stream in the direction of V_1 and normal to that direction.

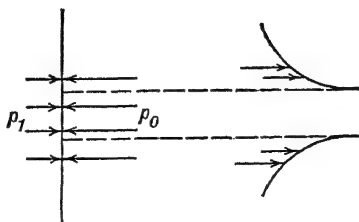
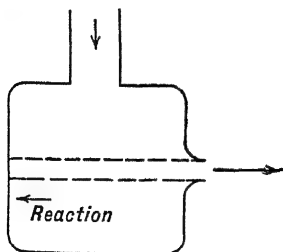


Derive corresponding expressions for the force necessary to hold the passage walls in place.

(b) Employing the data from (c) of problem 4 and assuming that $\alpha = 90^\circ$, find the magnitudes of the force components for which you derived expressions in (a). Show these as

vectors on a sketch of the passage and find the direction and magnitude of each of the resultant forces.

6. Derive an expression in terms of the velocity and flow for the reaction of a jet on a nozzle and its approach chamber, the reaction being the net force applied by the stream to the nozzle and chamber in the direction of the issuing stream. Assume that the stream enters the chamber in a direction perpendicular to that in which it leaves.



7. Show that for the reversible flow of an incompressible fluid the reaction can be accounted for by two forces that are identical in direction and magnitude: first, the

difference in pressure across the chamber wall opposite the nozzle opening, and second the difference between the pressures on the walls of the chamber around the nozzle opening and on the opposite walls. (It is only necessary to show that the first of these two forces is exactly one-half the reaction.)

8. (a) Find the reaction of a nozzle which expands steam reversibly and adiabatically from a large inlet chamber where its pressure is 100 lb/sq in. abs and its temperature 600 F to an exhaust space where the pressure is 60 lb/sq in. abs if the cross-sectional area of the stream is 1 sq in. where it reaches the exhaust pressure.

(b) A test on a nozzle having inlet conditions and exhaust pressure as stated above shows a rate of flow of 2.500 lb/sec and a reaction of 123.0 lb. What conclusions can you draw concerning the velocity of the jet?

9. A stream passing through a circular cross section in a duct has a velocity distribution which is given by the equation

$$V = V_r \left[1 - \left(\frac{r}{r_0} \right)^2 \right],$$

where V denotes the velocity of the stream at radius r from the center of the cross section, V_m the velocity at the center, and r_0 the radius at the wall. Assume the density of the fluid to be uniform. Find expressions for:

- (a) The momentum of the fluid which passes in unit time.
- (b) The velocity of a stream of uniform velocity which would have the same flow of momentum per unit time.
- (c) The kinetic energy of the fluid which passes in unit time.
- (d) The velocity of a stream of uniform velocity which would have the same flow of kinetic energy per unit time.

10. Show that at the state of maximum entropy on a Fanno line an infinitesimal change in enthalpy is given by the expression

$$dh = v dp.$$

11. For adiabatic flow in a pipe of uniform cross-sectional area derive the expression

$$p_s = \frac{(B-1)G}{B} \sqrt{\frac{2(h_0 - A)}{g(2B-1)}}$$

where p_s denotes the pressure at maximum entropy, G the flow per unit area, h_0 the enthalpy per unit mass in a large supply chamber ($= h + V^2/2g$), g the acceleration given to unit mass by unit force, and A and B the constants in the h - p - v relation ($h = A + Bpv$).

12. A test on the flow of steam through a piece of commercial 1-in. pipe made of wrought iron yielded the following data: For a section in the approach chamber, $a_1 = 0.089$ sq ft, $p_1 = 35.7$ lb/sq in. abs, $t_1 = 285$ F.

For three sections in the pipe

SECTION NUMBER	a sq ft	l ft	p lb/sq in. abs
2	0.00600	0	34.4
3	0.00600	32.2	25.1
4	0.00600	54.4	14.4

The distance l was measured along the pipe from section 2. The rate of steam flow was 10.50 lb/min. The pipe was well insulated, and the flow may therefore be considered to be adiabatic.

- (a) Find values for the constants A and B in the h - p - v relation,

$$h = A + Bpv,$$

from data on states in the neighborhood of state 1.

(b) Assume this relation to hold throughout the flow process, and compute values of the coefficient of friction and the Reynolds number corresponding to these data.

(c) Find the pressure corresponding to the point of maximum entropy: the lowest pressure to which expansion could proceed.

13. Assume a constant value of the friction factor $f (= R/\rho v^2)$ of 0.002 and compute and plot the flow of air through a converging nozzle with variation in the length of the *throat* of the nozzle. (The throat is the passage of uniform cross-sectional area the exit of which opens into the exhaust space.) The pressure is 100 lb/sq in. abs, and the temperature is 100 F, in the large chamber preceding the nozzle; the pressure is 40 lb/sq in. abs in the exhaust chamber. The throat is circular in cross section and 1 in. in diameter. Neglect friction in the converging portion.

14. (a) Plot on an h - s diagram the Fanno line for steam corresponding to a flow per unit area of 300 lb/sq ft sec and passing through the state for which the pressure is 200 lb/sq in. abs and the temperature is 700 F.

(b) Plot on the same diagram the Rayleigh line which passes through this state.

(c) Compute and plot the values of the pressures on the downstream side of a shock, as ordinates, against the pressure on the upstream side, as abscissas, for this Fanno line.

SYMBOLS

a	area
d	dimension of passage
f	coefficient of friction
F	force
g	acceleration given to unit mass by unit force
G	mass flow per unit area
h	enthalpy per unit mass
k	isentropic exponent
l	distance in direction of flow
L	distance between two sections
M	momentum per unit time
p	pressure
Q	heat to system
R	frictional force per unit area
Re	Reynolds number
s	entropy per unit mass
S	shear force per unit area
v	specific volume

V	volume, velocity
w	mass rate of flow
W	work
y	perimeter of passage
z	height

GREEK LETTERS

ρ	mass density of fluid
μ	coefficient of viscosity

SUBSCRIPTS

s	sound
t	throat of nozzle
x	component of vector in one direction

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CHAPTER XIX

SOME THERMODYNAMIC RELATIONS FOR THE PURE SUBSTANCE

The Maxwell Relations

It will be recalled that a pure substance is a system which is homogeneous in composition and invariable in its state of chemical aggregation. In the absence of motion, gravity, electricity, magnetism, and capillarity such a system is in a stable condition when it is homogeneous in state, for no spontaneous (irreversible) change can occur, such as a chemical reaction, an equalization of velocity, a change in height or shape in a gravitational field, etc.

If a unit mass of homogeneous pure substance executes a reversible process under the conditions prescribed above, the work for each step of the process is done by normal forces and is equal to $p dv$, and the heat for that step is given by $T ds$. Therefore, we may write

$$T ds = du + p dv,$$

or

$$du = T ds - p dv. \quad [15]$$

In previous chapters the properties h , ψ , and ζ have been defined as follows:

$$h = u + pv,$$

$$\psi = u - Ts,$$

and

$$\zeta = h - Ts.$$

Differentiating the first of these we get

$$dh = du + p dv + v dp.$$

From [15] we find that

$$du + p dv = T ds,$$

so that

$$dh = T ds + v dp. \quad [187]$$

By similar operations we get

$$d\psi = -p dv - s dT \quad [188]$$

and

$$d\zeta = v dp - s dT \quad [189]$$

Since du is an exact differential [or $u = f(s, v)$]

$$du = \left(\frac{\partial u}{\partial s} \right)_v ds + \left(\frac{\partial u}{\partial v} \right)_s dv.$$

If we compare this equation with [15] and note that ds may be zero when dv is not zero, and vice versa, we get

$$\left(\frac{\partial u}{\partial s} \right)_v = T \quad \text{and} \quad \left(\frac{\partial u}{\partial v} \right)_s = -p.$$

Since the order of differentiation is of no consequence in obtaining a second derivative, we have

$$\frac{\partial^2 u}{\partial s \partial v} = \frac{\partial^2 u}{\partial v \partial s}$$

or

$$\left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial p}{\partial s} \right)_v.$$

If we treat the differentials dh , $d\psi$, and $d\xi$ in [187], [188], and [189] in similar fashion we obtain three relations from each that are similar to those found from du . Collecting them, we have

$$\left(\frac{\partial u}{\partial s} \right)_v = T \quad [a], \quad \left(\frac{\partial u}{\partial v} \right)_s = -p \quad [b], \quad \left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial p}{\partial s} \right)_v \quad [c] \quad [190]$$

$$\left(\frac{\partial h}{\partial s} \right)_p = T \quad [a], \quad \left(\frac{\partial h}{\partial p} \right)_s = v \quad [b], \quad \left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial v}{\partial s} \right)_p \quad [c] \quad [191]$$

$$\left(\frac{\partial \psi}{\partial v} \right)_T = -p \quad [a], \quad \left(\frac{\partial \psi}{\partial T} \right)_v = -s \quad [b], \quad \left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v \quad [c] \quad [192]$$

$$\left(\frac{\partial \xi}{\partial p} \right)_T = v \quad [a], \quad \left(\frac{\partial \xi}{\partial T} \right)_p = -s \quad [b], \quad \left(\frac{\partial s}{\partial p} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_p \quad [c] \quad [193]$$

The [c] group of equations are of importance in the formulation of properties of pure substances because they relate the entropy to the pressure, volume, and temperature. They are known as the *Maxwell relations*.

A less rigorous graphic proof of [190c] might serve to coordinate the Maxwell relations with simpler concepts.

Let a system comprising a pure substance execute reversibly a small cycle 1-2-3-4-1 consisting of two isometrics different in specific vol-

ume by amount dv and two isentropics different in entropy by amount ds . Let the process 1-2 be an isometric rise in pressure corresponding to the volume v and the process 3-4 an isometric fall in pressure corresponding to the volume $(v + dv)$ (Fig. 161). Let processes 2-3 and 4-1 be isentropics. If the cycle 1-2-3-4-1 is executed reversibly by the system the net work of the cycle ($\oint dW$) will be equal to the area 1-2-3-4-1 on the p - v diagram. For the cycle described the net work and the area 1-2-3-4-1 are greater than zero because the process follows the path 1-2-3-4-1 in a clockwise direction.

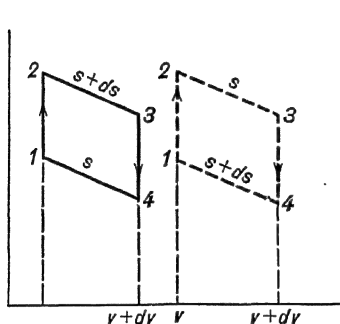


FIG. 161

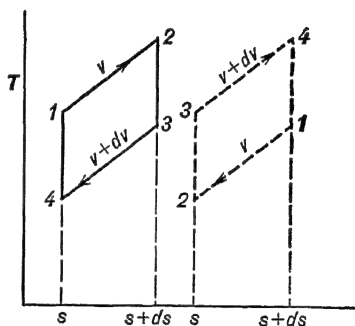


FIG. 162

Graphical Proof of a Maxwell Relation

On the T - s diagram (Fig. 162) the area enclosed by the lines representing the cycle is equal to the net heat of the cycle ($\oint dQ$). By the First Law the net heat and the net work are identical in magnitude and sign:

$$\oint dQ = \oint dW.$$

Therefore, the area 1-2-3-4-1 on the T - s diagram must be identical in magnitude with the area 1-2-3-4-1 on the p - v diagram; moreover, if the cycle proceeds in the clockwise sense on the p - v diagram it must proceed in the clockwise sense on the T - s diagram. If the process 2-3 is the isentropic of higher entropy ($s + ds$), then the cycle must be as shown by solid lines in Figs. 161 and 162. If process 2-3 is the isentropic of lower entropy (s), then the cycle must be as shown by the dash lines. These are the only possible arrangements for clockwise rotation.

Let us consider the solid lines. The increase in pressure between states 1 and 2 (and also that between 4 and 3 to small quantities of the first order) is given by

$$\left(\frac{\partial p}{\partial s}\right)_v ds,$$

so that the area 1-2-3-4-1 on the p - v diagram is given by

$$\left(\frac{\partial p}{\partial s}\right)_v ds dv.$$

The increase in temperature between states 1 and 4 (and also that between 2 and 3) is given by

$$-\left(\frac{\partial T}{\partial v}\right)_s dv$$

(the minus sign indicating that as the volume increases the temperature decreases), so that the area 1-2-3-4-1 on the T - s diagram is given by

$$-\left(\frac{\partial T}{\partial v}\right)_s dv ds.$$

Since the areas on the two diagrams must be identical in magnitude and sign, it follows that

$$\left(\frac{\partial p}{\partial s}\right)_v ds dv = -\left(\frac{\partial T}{\partial v}\right)_s dv ds,$$

or simply

$$\left(\frac{\partial p}{\partial s}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_s.$$

This is the Maxwell relation [190c]. The same result will be obtained if the cycle is represented by the dash lines of Figs. 161 and 162.*

Each of the four Maxwell relations can be proved in a similar fashion by describing a cycle consisting of pairs of lines along which the properties corresponding to the subscripts of the relation are respectively constant.

* It may be noted from these figures that, if a system becomes cooler upon isentropic expansion (solid line 2-3, Fig. 162), then its pressure will rise if it is heated at constant volume (solid line 1-2, Fig. 161, the increase in entropy denoting a flow of heat to the system). If a system becomes hotter upon isentropic expansion, then its pressure will fall if it is heated at constant volume (dash lines of Figs. 161 and 162). These relations are derived more rigorously in Chapter XXIII.

Derivatives of the Specific Heats

By choosing equivalent pairs of derivatives from relations [a] and [b] above we get four useful equations:

$$\left. \begin{aligned} \left(\frac{\partial u}{\partial s}\right)_v &= \left(\frac{\partial h}{\partial s}\right)_p, \\ \left(\frac{\partial u}{\partial v}\right)_s &= \left(\frac{\partial \psi}{\partial v}\right)_T, \\ \left(\frac{\partial h}{\partial p}\right)_s &= \left(\frac{\partial \xi}{\partial p}\right)_T, \\ \left(\frac{\partial \psi}{\partial T}\right)_v &= \left(\frac{\partial \xi}{\partial T}\right)_p. \end{aligned} \right\} \quad [194]$$

and

Other relations can be obtained from the same source. For example, the specific heats may be expressed in terms of the entropy:

$$\left(\frac{\partial u}{\partial s}\right)_v = T, \quad \therefore c_v = \left(\frac{\partial u}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v, \quad [195]$$

and

$$\left(\frac{\partial h}{\partial s}\right)_p = T, \quad \therefore c_p = \left(\frac{\partial h}{\partial T}\right)_p = T \left(\frac{\partial s}{\partial T}\right)_p. \quad [196]$$

Derivatives of the specific heats are, of course, second derivatives of properties:

$$\left(\frac{\partial c_v}{\partial v}\right)_T = \frac{\partial^2 s}{\partial T \partial v}.$$

But

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v, \quad [192c]$$

Therefore

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T \frac{\partial^2 s}{\partial T \partial v} = T \left(\frac{\partial^2 p}{\partial T^2}\right)_v. \quad [197]$$

Similarly,

$$\left(\frac{\partial c_p}{\partial p}\right)_T = T \frac{\partial^2 s}{\partial T \partial p} = -T \left(\frac{\partial^2 v}{\partial T^2}\right)_p. \quad [198]$$

These last equations are useful when adequate information on the p - v - T relation is accompanied by meager data on the specific heat.

Coefficients in h , p , and T

The relation between the partial first derivatives of any three properties is given by the proposition from the calculus

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1, \quad [199]$$

which may be proved as follows:

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz, \quad [A]$$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz. \quad [B]$$

Substitution of [B] in [A] gives

$$\begin{aligned} dx &= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x dz + \left(\frac{\partial x}{\partial z}\right)_y dz \\ &= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y \right] dz. \end{aligned}$$

Since dz may be zero when dx is not (that is, x and z are independent variables), it follows that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1,$$

which is a familiar relation from the calculus. Since dx may be zero when dz is not,

$$\left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y \right] dz = 0.$$

Dividing through by $(\partial x/\partial z)_y dz$ we get the desired equation

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \quad [200]$$

This proposition will be applied frequently in subsequent discussions. An example of its use is afforded by the three derivatives of h , p , and T : namely, the specific heat at constant pressure, $c_p = \left(\frac{\partial h}{\partial T}\right)_p$, the Joule-Thomson coefficient, $\mu = \left(\frac{\partial T}{\partial p}\right)_h$, and the constant-temperature coefficient, $c = \left(\frac{\partial h}{\partial p}\right)_T$. According to [199] these three must be related

in the form

$$\left(\frac{\partial h}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_h \left(\frac{\partial T}{\partial h}\right)_p = -1,$$

or

$$c = -\mu c_p \quad [201]$$

This relation is frequently used in comparing experimental data from various sources.

Only a few of the many interesting and useful relations between the quantities p , v , T , s , u , h , ψ , and ζ have been derived from the First and Second Laws in the preceding paragraphs. The equation best suited to any particular purpose can be derived from one of those given above, or it may be taken from some more comprehensive tabulation such as that of Bridgman.*

The Clapeyron Relation

If the third Maxwell relation

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

is applied to a mixture of two phases of a pure substance, it is found that the derivative $(\partial s/\partial v)_T$ can be expressed as a ratio of the change of entropy during the change in phase at constant temperature to the corresponding change of volume; thus

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{s_1 - s_2}{v_1 - v_2},$$

where subscripts 1 and 2 refer respectively to saturated states of the two phases. Because the pressure is a function only of temperature as long as both phases are present, we may substitute the derivative of the pressure-temperature relation for the other partial derivative in the Maxwell equation. Making both substitutions we get

$$\frac{s_1 - s_2}{v_1 - v_2} = \frac{dp}{dT};$$

or, since $(\partial h/\partial s)_p = T$,

$$\frac{h_1 - h_2}{v_1 - v_2} = T \frac{dp}{dT}. \quad [202]$$

This equation is known as the Clapeyron relation. It links three commonly measured quantities, namely, pressure of two phases in

* *A Condensed Collection of Thermodynamic Formulas*, P. W. Bridgman, Harvard University Press.

equilibrium, latent heat, and expansion during change of phase. It is frequently used to compute one of the three when the other two have been measured.

The graphical proof used for the Maxwell relations may be applied to the Clapeyron relation. Let a system consisting of a pure substance describe a reversible cycle comprising two isothermal processes extending between the saturation states of two phases that can coexist (Fig. 163). Let these two processes be separated in pressure by dp

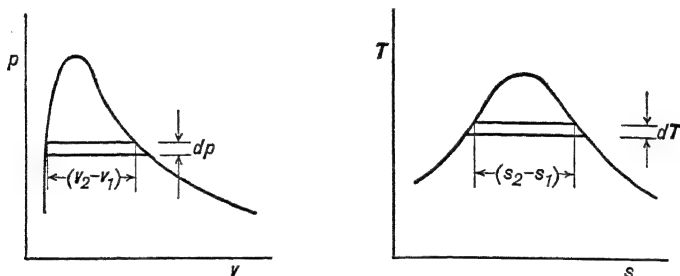


FIG. 163. Graphical Proof of the Clapeyron Relation

and in temperature by the corresponding dT . The cycle may be closed by paths coinciding with the saturation curves. By the First Law

$$dQ = \oint dW.$$

Then the area enclosed by the cycle on the T - s diagram is equal to the area it encloses on the p - v diagram; or, to small quantities of the first order,

$$(s_1 - s_2) dT = (v_1 - v_2) dp.$$

Therefore

$$\frac{s_1 - s_2}{v_1 - v_2} = \frac{dp}{dT}.$$

PROBLEMS

1. Show that all lines of constant pressure on a Mollier (enthalpy-entropy) chart must have the same slope at the same temperature. Verify this by means of a parallel ruler and a Mollier chart for steam.

Show that a line of constant pressure on a Mollier chart must be concave upward.

On what kind of chart would the slope of the lines of constant temperature be given by the pressure?

2. Show that the increase in kinetic energy per unit decrease in pressure in reversible steady flow is equal to the specific volume of the fluid.

3. Employing only the relation

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

and the first Maxwell relation, derive the remaining three Maxwell relations.

4. Derive each of the Maxwell relations graphically, and justify it for both positive and negative values of one of the partial derivatives.

5. Find approximate values for the derivatives of the fourth Maxwell relation [193c] for steam at 500 lb/sq in. abs and 700 F. Are they in accord with the Maxwell relation?

Do the same for the three other Maxwell relations.

6. Discuss the significance of each of the Maxwell relations in the two-phase region.

7. Noting that from the h - p - T relation we get $c = -\mu c_p$, find a corresponding equation from the u - v - T relation.

8. Note from Fig. 18 that at a pressure of 1 atmosphere the melting temperature of ice decreases with increase in pressure, whereas at a pressure of 3000 atmospheres the melting temperature increases with increase in pressure. What do these facts indicate concerning the change in volume of ice during fusion?

The same figure shows that the boundary between ice I and ice III on a temperature-pressure diagram is nearly vertical. What does this indicate as regards the latent heat and the expansion corresponding to a change from ice I to ice III?

9. At the triple point water has the following values of its properties:

PRESSURE	TEMPERATURE	PHASE	ENTHALPY	SPECIFIC VOLUME
lb/sq in. abs	F	Liquid	0.02	0.01602
	32.02	Solid	-143.3	0.01747

Assume that the changes in enthalpy and specific volume are independent of the pressure, and calculate the melting temperature at a pressure of 1000 atmospheres. Compare this value with an approximate one obtained from Fig. 18.

10. Show that for a perfect gas the rate of change of the vapor pressure (saturation pressure) with temperature is given by the equation

$$\frac{d(\ln p)}{dT} = \frac{h_{fg}}{RT^2},$$

provided that the volume of the liquid phase is negligible compared with the volume of the gas phase.

11. Dühring's rule states that if the saturation temperature of a substance A is plotted against that of substance B for the same values of the pressure the result is approximately a straight line. Test this rule by means of data on ammonia and water between 5 and 20 lb/sq in. abs.

Derive an expression for the slope of the Dühring line in terms of saturation properties of substances A and B . Confirm this relation for ammonia and water.

SYMBOLS

c	constant-temperature coefficient $(\partial h / \partial p)_t$
c_p	specific heat at constant pressure
c_v	specific heat at constant volume
h	enthalpy per unit mass
p	pressure
Q	heat to system
s	entropy per unit mass
T	absolute temperature
u	internal energy of unit system in the absence of motion, gravity, etc.
v	specific volume
W	work done by system

GREEK LETTERS

μ	Joule-Thomson coefficient $(\partial T / \partial p)_h$
ψ	$(u - Ts)$
ζ	$(h - Ts)$

SUBSCRIPTS

h	constant enthalpy
p	constant pressure
s	constant entropy
t	constant temperature
v	constant volume

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CHAPTER XX

THE RELATION BETWEEN PRESSURE, VOLUME, AND TEMPERATURE, AND ITS DEVELOPMENT

The p - v - T Relation

At very low pressures relative to the critical pressure or at very high temperatures relative to the critical temperature the p - v - T relation for a gas is given by the equation

$$pv = RT, \quad [18]$$

where R is a constant which may be found by dividing the universal gas constant R by the molecular weight of the gas (see Chapter IX). In accordance with [18] the specific volume is infinite at zero pressure for any finite temperature and at infinite temperature for any finite pressure. For this reason the volume is an unsatisfactory coordinate for a chart of properties extending over a wide range of conditions. On the other hand, the quantity pv/RT remains finite for all finite pressures and is unity at zero pressure and at infinite temperature. It is therefore commonly employed as a coordinate when the p - v - T relation is to be illustrated.

When the quantity pv/RT , which we shall denote by μ , is plotted against pressure for any one pure substance, charts like Figs. 166 and 167 are obtained. Besides having $\mu = 1$ at $p = 0$ and at $T = \infty$ similar charts for all substances would have the following characteristics in common: the value of μ at the critical point is in the neighborhood of 0.3; lines of constant temperature all lie between two envelopes, one at the top and the other at the bottom of the diagram; lines of constant temperature approach zero pressure with finite slope and with decreasing curvature.

Equations of State

The p - v - T relation is often stated in the form of an equation which is called an *equation of state*. An equation of state may be devised, with all constants in numerical form, for the purpose of representing the p - v - T relation for a specific substance; or it may be devised with the constants indicated by symbols (for which different sets of numbers would be substituted for different substances) for the purpose of rep-

representing the p - v - T relation for all substances or for a group of substances. The equation of state given on page 15 of the *Steam Tables* of Keenan and Keyes is an example of the specific type. It represents to high precision the properties of water vapor over a limited range of conditions. An equation of such high precision can be produced only with the aid of an extensive body of experimental data of high quality.

For substances about which less is known the general type of equation of state will serve for interpolation between experimental quantities and for extrapolation beyond them. A few equations of state of this type are discussed below.

The van der Waals Equation

The equation proposed by van der Waals in 1873 is of historical importance and of some practical utility. It represents in a qualitative way both liquid and vapor phases. For example, the μ - p chart corresponding to the equation of van der Waals has a value of μ of 0.375 at the critical point, somewhat higher than that for actual substances, but of the same order of magnitude; its lines of constant temperature lie between two envelopes, one at the top and the other at the bottom of the diagram; its lines of constant temperature approach zero pressure with finite slope and with decreasing curvature. In these ways and in many others the equation of van der Waals indicates the characteristics of real substances even though it does not represent the values of properties with precision. In fact no equation of state of any reasonable degree of complexity has yet been proposed which represents with precision the properties of both liquid and vapor phases.

The equation of van der Waals is usually written

$$p = \frac{RT}{v - b} - \frac{a}{v^2}, \quad [203]$$

where a and b are constants for any one substance. Isotherms from [203] are shown in Fig. 164. Below a certain temperature T_c each isotherm passes through a maximum and a minimum, the positions of which can be found by equating the appropriate derivative to zero. The locus of these maxima and minima is shown by the dash curve in Fig. 164 which represents the equation

$$= \frac{a}{v^2} \left[\frac{2(v - b)}{v} - 1 \right]. \quad [204]$$

For the isotherm which is tangent to the highest point on this curve the maximum and minimum points coincide in a point of inflection c at which both $(\partial p / \partial v)_T$ and $(\partial^2 p / \partial v^2)_T$ are zero. The position of this

point is found by equating the derivative of [204] to zero. Using the subscript c to distinguish the properties at the point in question, we have

$$v_c = 3b, \quad [205]$$

and, by substitution in [204] and [203]

$$p_c = \frac{a}{27b^2} \quad [206]$$

and

$$\frac{8a}{27Rb} \quad [207]$$

At any temperature below T_c the portion of the isotherm to the left of the minimum point represents liquid states and that to the right of the maximum point vapor states. The portion of the curve between the

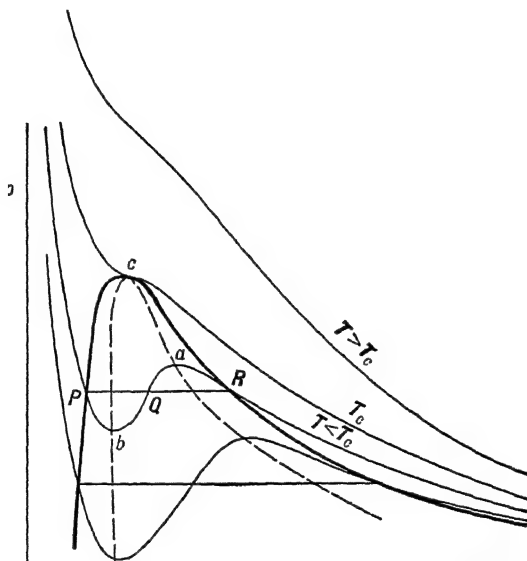


FIG. 164. The Equation of State of van der Waals

maximum and minimum represents unstable states for which any slight accidental decrease in volume would cause a decrease in pressure and consequent collapse of the fluid to a more stable state.*

Liquid and vapor states that can coexist in equilibrium must be at the same pressure. Furthermore, since the two states may be present

* It is shown in Chapter XXIV that the condition $(\partial p / \partial v)_T < 0$ is necessary for stability of a substance.

in any proportions it is possible to bring about a change of state at constant pressure and at constant temperature from one phase to the other (PQR , Fig. 164). At the same temperature there is a path of constant temperature $RaQbP$ by which the fluid can return to its original state. Since this cycle of operations can occur reversibly at one level of temperature it is necessary according to the Second Law that the net work done by the system should be zero. Therefore we may write

$$\oint p \, dv = 0.$$

It follows that the area $PQbP$ must be equal to the area $QaRQ$. Through this requirement the saturation states (PcR , Fig. 164) can be identified. The points lying between P and b represent states of the liquid for which the temperature exceeds the saturation temperature corresponding to the pressure (superheated liquid), and the points between a and R represent states of the vapor for which the temperature is less than the saturation temperature (supersaturated or undercooled vapor). Both are metastable conditions,* that is, stable for small disturbances but unstable for large ones.

The state corresponding to the point c can now be identified with the liquid-vapor critical point, and p_c , T_c , and v_c are the values of the corresponding properties at the critical point. From [205] it can be seen that the critical volume suffices to determine the constant b , and from [206] and [207] that any pair of the critical values p_c , v_c , and T_c completely determine the constants a and b and the remaining critical value. From [205], [206], and [207] we find that the value of μ at the critical state is independent of the magnitudes of the constants:

$$\mu_c = \frac{p_c v_c}{RT_c} = \frac{3}{8}.$$

Table VIII (prepared by Weber) shows that for actual substances μ_c ranges between 0.2 and 0.3, virtually none being as large as the value given by van der Waals' equation.

Though the constants a and b may be determined by any pair of the quantities p_c , v_c , and T_c , they need not be so determined. By alteration of their magnitudes the equation may be made to accord better with measured values of the properties in a selected region. It should be noted, however, that for any finite values of the constants the van der Waals equation reduces to the form

$$pv = RT$$

for zero pressure and for infinite temperature.

* See page 425.

TABLE VIII
 CRITICAL CONSTANTS *

 From Weber, *Thermodynamics for Chemical Engineers*, Wiley, 1939, p. 110

Gas	Formula	Molecular Weight	T_c		P_c atm	ρ_c g/cm ³	V_c liters/ mole	$\frac{RT_c}{P_c V_c}$
			K	F abs				
Acetic acid	C ₂ H ₄ O ₂	60.03	594.8	1070.6	57.2	0.351	0.171	4.99
Acetylene	C ₂ H ₂	26.02	309	556	62	0.231	0.113	3.63
Ammonia	NH ₃	17.03	405.56	730.01	111.5	0.235	0.0724	4.12
Argon	A	39.94	151	272	48	0.531	0.0753	3.44
Benzene	C ₆ H ₆	78.05	561.7	1011.1	47.7	0.304	0.257	3.76
Butane	C ₄ H ₁₀	58.08	425.17	765.31	37.48	0.2254	0.2576	3.61
Carbon dioxide	CO ₂	44.00	304.26	547.67	73.0	0.460	0.0957	3.58
Carbon monoxide	CO	28.00	132.98	239.36	34.53	0.3010	0.0930	3.40
Carbon tetra- chloride	CCl ₄	153.83	556.3	1001.3	45.0	0.558	0.276	3.69
Chlorine	Cl ₂	70.91	417.2	751.0	76.1	0.573	0.124	3.64
Decane	C ₁₀ H ₂₂	142.17	619.4	1115	21.24	0.2327	0.611	3.91
Ethane	C ₂ H ₆	30.05	305.40	549.72	48.20	0.2032	0.148	3.51
Ethanol	C ₂ H ₅ OH	46.05	516.2	929.2	63.1	0.275	0.167	4.01
Ethyl chloride	C ₂ H ₅ Cl	64.50	460.4	828.7	52	0.33	0.196	3.73
Ethyl ether	C ₂ H ₅ O	74.08	466.0	838.8	35.5	0.263	0.282	3.82
Ethylene	C ₂ H ₄	28.03	282.8	509.0	50.9	0.22	0.127	3.58
Helium	He	4.00	5.26	9.47	2.26	0.0693	0.058	3.28
Heptane	C ₇ H ₁₆	100.12	540.17	972.31	27.00	0.2433	0.411	3.99
Hexane	C ₆ H ₁₄	86.11	507.9	914.3	29.63	0.2344	0.367	3.82
Hydrogen	H ₂	2.02	33.3	59.9	12.8	0.0310	0.065	3.27
Hydrogen cyanide	HCN	27.02	456.7	822.1	50	0.20	0.135	5.54
Methane	CH ₄	16.03	190.7	343.3	45.8	0.162	0.099	3.46
Methanol	CH ₃ OH	32.03	513.2	923.8	98.7	0.272	0.118	4.01
Methyl chloride	CH ₃ Cl	50.48	416.3	749.3	65.8	0.37	0.136	3.81
Neon	Ne	20.18	44.46	80.03	25.9	0.484	0.417	3.37
Nitric oxide	NO	30.01	179	323	65	0.52	0.0578	3.92
Nitrogen	N ₂	28.02	126.1	227.0	33.5	0.3110	0.0900	3.43
Nonane	C ₉ H ₂₀	128.16	596	1072	22.86	0.2319	0.553	3.86
Octane	C ₈ H ₁₈	114.14	569.4	1024.9	24.66	0.2327	0.490	3.85
Oxygen	O ₂	32.00	154.4	277.9	49.7	0.430	0.0744	3.42
Pentane	C ₅ H ₁₂	72.09	470.3	846.6	33.04	0.2323	0.310	3.77
Propane	C ₃ H ₈	44.06	369.97	665.95	42.01	0.2260	0.195	3.71
Sulphur dioxide	SO ₂	64.06	430.4	774.7	77.7	0.52	0.123	3.71
Sulphur trioxide	SO ₃	80.06	491.5	884.7	83.6	0.630	0.127	3.80
Toluene	C ₇ H ₈	92.06	593.8	1068.8	41.6	0.292	0.315	3.71
Water	H ₂ O	18.02	647.30	1165.14	218.53	0.3183	0.05656	4.30

 * Compiled from various sources, especially *International Critical Tables*, Vol. 3, pp. 248-249, and Landolt-Börnstein's *Physikalisch-Chemische Tabellen*, Vol. IIIa, p. 246, 1935.

The Beattie-Bridgman Equation

We shall not attempt to list the numerous equations of state that have been proposed since the appearance of the equation of van der Waals. Most of them have been intended to represent vapors at low pressures relative to the critical pressure, though a few have been expressly designed for pressures of the order of the critical pressure.

We shall mention only the equation of Beattie and Bridgman because it has proved to be of great utility in formulating the properties of the vapor phase of many substances at pressures less than the critical pressure.* It is as follows:

$$p = \frac{RT(1 - \epsilon)}{v^2} (v + B) - \frac{A}{v^2} \quad [208]$$

where $A = A_0(1 - a/v)$, $B = B_0(1 - b/v)$, $\epsilon = c/vT^3$, and A_0 , a , B_0 , b , and c are constants which are different for different gases. Their values for several substances are given in Table IX.

TABLE IX

CONSTANTS OF THE BEATTIE AND BRIDGMAN EQUATION OF STATE¹

for pressure in atm, volume in liters/g mole, temperature in deg K

 $R = 0.08206$ atm liters/g mole K

Gas	A_0	a	B_0	b	$10^{-4}c$
Helium	0.0216	0.05984	0.01400	0.0	0.0040
Neon	0.2125	0.02196	0.02060	0.0	0.101
Argon	1.2907	0.02328	0.03931	0.0	5.99
Hydrogen	0.1975	-0.00506	0.02096	-0.04359	0.0504
Nitrogen	1.3445	0.02617	0.05046	-0.00691	4.20
Oxygen	1.4911	0.02562	0.04624	+0.004208	4.80
Air	1.3012	0.01931	0.04611	-0.001101	4.34
CO ₂	5.0065	0.07132	0.10476	0.07235	66.00
(C ₂ H ₅) ₂ O	31.278	0.12426	0.45446	0.11954	33.33
C ₂ H ₄	6.152	0.04964	0.12156	-0.03597	22.68
Ammonia	2.3930	0.17031	0.03415	0.19112	476.87
CO	1.3445	0.02617	0.05046	-0.00691	4.20
N ₂ O	5.0065	0.07132	0.10476	0.07235	66.0
CH ₄	2.2769	0.01855	0.05587	-0.01587	12.83
C ₂ H ₆	5.8800	0.05861	0.09400	0.01915	90.00
C ₃ H ₈	11.9200	0.07321	0.18100	0.04293	120
<i>n</i> -C ₄ H ₁₀	17.794	0.12161	0.24620	0.09423	350
<i>n</i> -C ₇ H ₁₆	54.520	0.20066	0.70816	0.19179	400

¹ *Proc. Am. Acad. Arts & Sci.*, Vol. 63 (1928), pp. 229-308; *Z. Physik*, Vol. 62 (1930), pp. 95-101; *Journal Chemical Physics*, Vol. 3 (1935), pp. 93-96; *Journal American Chemical Society*, Vol. 59 (1937), pp. 1587-1589, 1589-1590; Vol. 61 (1939), pp. 26-27.

* *Proc. Am. Acad. Arts and Sci.*, Vol. 63 (1928), pp. 229-308. The equation appears to be suitable for volumes greater than twice the critical volume.

A Generalized Form of the Equation of State

It was mentioned above that the isotherms on a μ - p chart have finite slope and decreasing curvature as they approach zero pressure. This characteristic suggests an equation of state of the form

$$\frac{pv}{RT} = 1 + \alpha_1 p + \sum \alpha_i p^i, \quad [209]$$

where each α is a function of temperature only and $\sum \alpha_i p^i$ denotes a series of terms for each of which the exponent i is greater than 1. This is the type of equation employed by Keyes (and given on page 15 of the *Steam Tables*) in formulating the properties of steam for volumes in excess of three times the critical volume. The precision and the range of applicability of such an equation depend largely on the number of terms in the group $\sum \alpha_i p^i$. Keyes used three.

It should be noted that this form of the equation of state can be solved explicitly for v as a function of p and t , whereas the equations of van der Waals and of Beattie and Bridgman cannot. Since p and t are the properties most readily measured it is a convenience to have them as independent variables in the equation of state. This is a matter of even greater consequence when internal energy, enthalpy, and entropy are to be evaluated and tabulated.

The values of i in [209] are often successively 2, 3, etc. By a series type of transformation various equations of state may be reduced to this form. For example, the Beattie-Bridgman equation is approximately reproduced by the equation

$$\frac{pv}{RT} = 1 + \frac{\beta}{R^2 T^2} p + \frac{\gamma}{R^3 T^3} p^2 + \frac{\delta}{R^4 T^4} p^3 *$$

where

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2}, \quad \gamma = -RTB_0b + A_0a - \frac{RB_0c}{T^2},$$

$$\delta = \frac{RB_0bc}{T^2}.$$

The Generalized p - v - T Relation

The similarity between the p - v - T relations for various substances which has been indicated in the preceding paragraphs has given rise to various rules and methods by which the properties of a given substance

* Scatchard gives a similar equation with more involved coefficients for the terms in p , p^2 , and p^3 . At high pressures it is a distinctly better approximation to [208]. *Proc. Nat. Acad. Sci.*, Vol. 16 (1930), pp. 811-813.

may be estimated on the basis of a limited amount of empirical data. Some of these rules and methods are described below.

The Law of Corresponding States

The Law of Corresponding States declares that there is a single functional relationship of the form

$$v_R = f(p_R, T_R), \quad [210]$$

which holds for all substances. In this statement v_R is the ratio of the volume at p and T to the volume at the critical state, p_R is the ratio of the pressure p to the critical pressure, and T_R is the ratio of the temperature T to the critical temperature. The quantities v_R , p_R , and T_R are called respectively the *reduced volume*, the *reduced pressure*, and the *reduced temperature*.

If the Law of Corresponding States were true, values of p_R plotted against values of T_R for any one value of v_R would yield a single curve for all substances. The data for a series of such curves are plotted in Fig. 165 for a group of hydrocarbons at pressures and temperatures that are high relative to the critical pressure and temperature. The critical pressures of these substances vary from 27 to 51 atmospheres and the critical temperatures from 191 to 540 K. It can be seen, therefore, that a wide range of values has been brought into a fair degree of concordance by means of the reduced properties. If the values of the pressure, temperature, and specific volume at the critical point for any one of these gases are known the entire p - v - T relation at high pressures and temperatures can be found from Fig. 165 to a precision of about 10 per cent. This precision would be satisfactory for certain rough calculations.

At low pressures the Law of Corresponding States loses all validity. Since v_R is, by [210], a single function of p_R and T_R , it follows that $p_R v_R / T_R$ also is a single function of p_R and T_R for all gases. There is, therefore, at any one value of T_R a single value of $p_R v_R / T_R$ at zero pressure. The value of μ (or pv/RT) may be expressed in terms of this quantity; thus

$$= \left(\frac{p_R v_R}{T_R} \right) \left(\frac{p_c v_c}{RT_c} \right).$$

The value of the first factor in the right-hand member is fixed by [210], but the value of the second factor may range at least from 0.18 to 0.3 according to the data of Table VIII. It is known, however, that the value of μ at zero pressure is unity for all gases; therefore, [210] cannot hold.

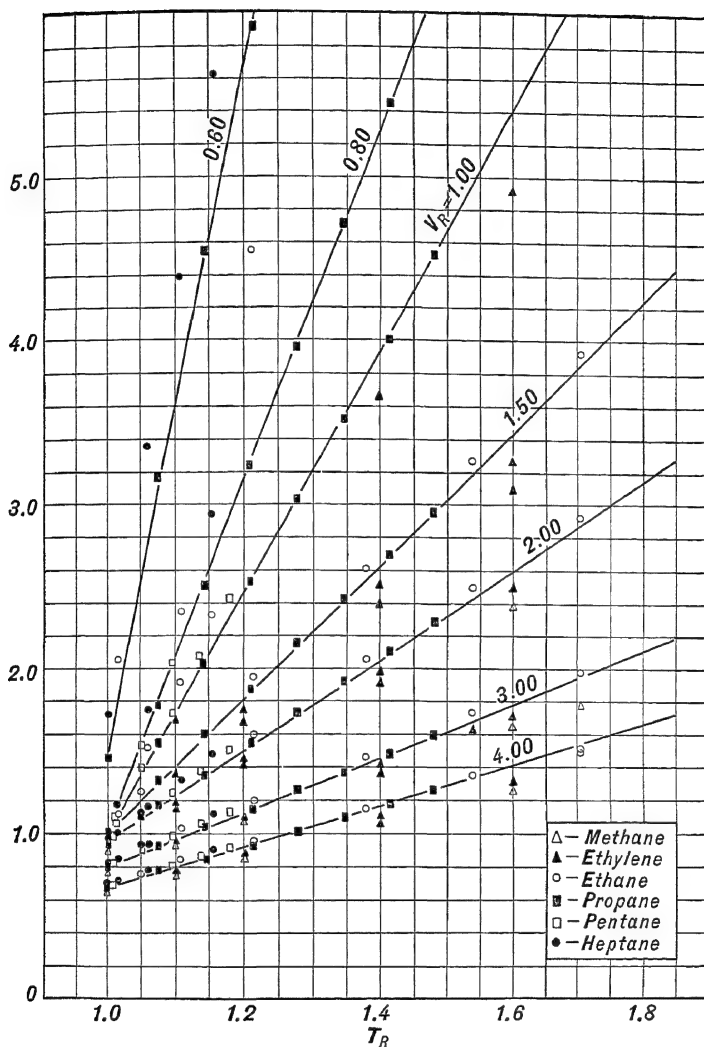
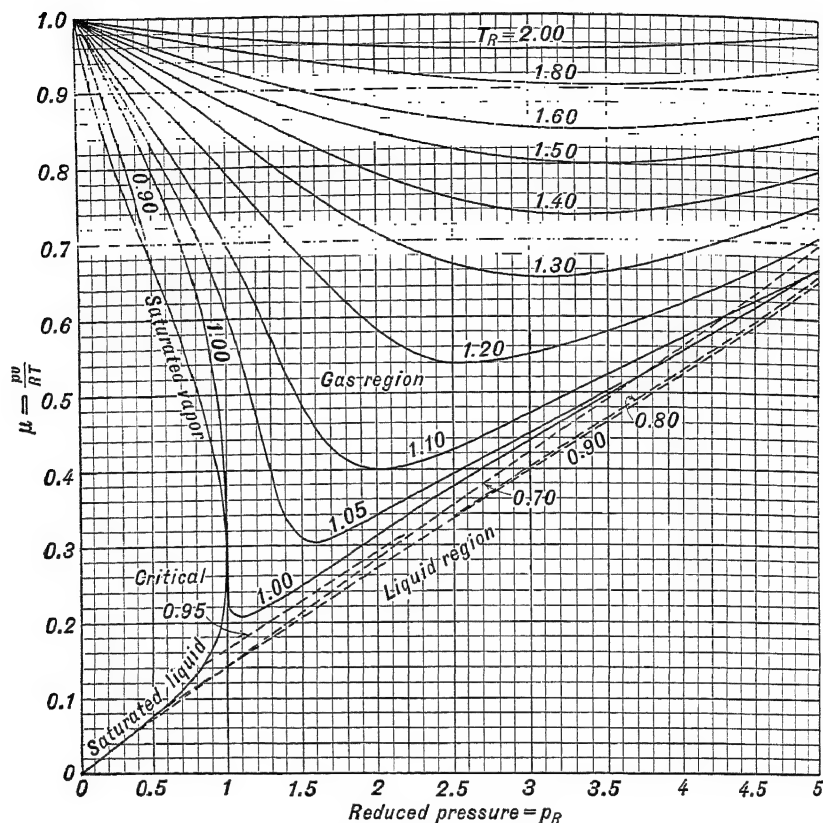


FIG. 165. Reduced Isometrics

From W. C. Kay, Sc.D. Thesis, M.I.T., 1937, p. 68.

The Generalized μ Chart

The similarity of pattern of the μ - p charts for different substances suggests that this chart may be generalized by substituting p_R for p and T_R for T . Then all isotherms must converge on the same point at zero pressure, and the critical point must lie on the same value of the

FIG. 166. The Generalized μ Chart

From Weber.*

abscissa for all substances. Two such charts (Figs. 166 and 167) have been prepared by Weber* from the data of Su.† At pressures that are low relative to the critical pressure and at temperatures that are high relative to the critical temperature, these charts will give results far superior to those of the Law of Corresponding States; but near the critical point the latter is preferable.

The p - v - T Relation for Mixtures

The Gibbs-Dalton Law provides a means of combining information concerning the various constituents of a mixture of gases to obtain relations between the properties of the mixture. It states that the

* Weber, *Thermodynamics for Chemical Engineers*, Wiley, 1939, pp. 108, 109.

† Su, Sc.D. Thesis, M.I.T., 1937, p. 50.

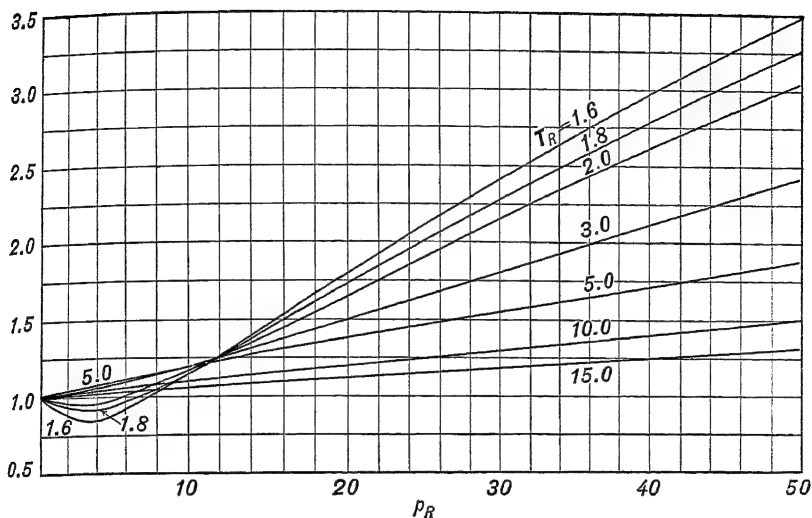


Fig. 167. The Generalized μ Chart at High Pressures and Temperatures
From Weber.

pressure of a mixture is given by the equation

$$p = p_1 + p_2 + \cdots p_n, \quad [85]$$

under conditions such that

$$T = T_1 = T_2 = \cdots T_n$$

and

$$V = V_1 = V_2 = \cdots V_n.$$

In these equations p , V , and T denote respectively the pressure, volume, and temperature of the mixture, and the same symbols with subscripts refer to the constituents 1, 2, \cdots n of the mixture when each is separate from all the others.

The Gibbs-Dalton Law is used more frequently than any other rule for combining the properties of constituents to get the properties of a mixture. At low pressures relative to the critical pressure it will usually give the properties of the mixture to a precision approximating that of the data of the constituents. However, at higher pressures it becomes quite unreliable and must be supplanted by some more precise device.

Gilliland's Method

The isometrics of a gas are nearly straight when plotted on a pressure-temperature diagram (see Fig. 165) and, therefore, may be approximated by the equation

$$p = \phi_1 T - \phi_2,$$

where ϕ_1 and ϕ_2 for any one gas are functions of volume only. Gilliland has proposed* that the quantities ϕ_1 and ϕ_2 for the constituents of a mixture be combined according to certain rules to get the corresponding quantities for the mixture. The former is found from the equation

$$\phi_1 = x_a\phi_{1a} + x_b\phi_{1b} + \dots \quad [211]$$

where ϕ_1 denotes the slope of an isometric of the mixture; x_a, x_b , etc., denote the mole fractions of constituents a, b , etc., in the mixture; and

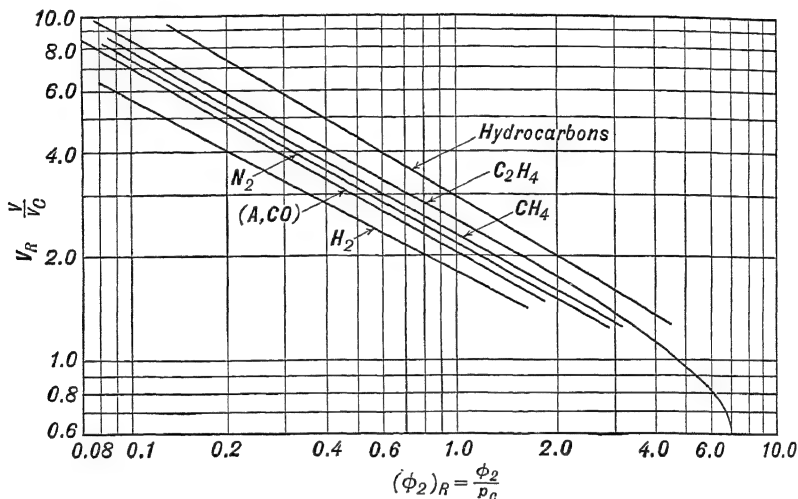


FIG. 168. Values of ϕ_2

From Gilliland, *Industrial and Engineering Chemistry*, Vol. 28 (1936), pp. 212-215.

ϕ_{1a}, ϕ_{1b} , etc., denote the slopes of isometrics of the pure constituents when each has the same number of moles per unit volume as the mixture itself (not the same as the constituent in the mixture). The corresponding equation for the intercept ϕ_2 is

$$\phi_2 = [x_a\sqrt{\phi_{2a}} + x_b\sqrt{\phi_{2b}} + \dots]^2, \quad [212]$$

where the symbols are analogous to those in [211]. Gilliland gives the values of ϕ_2 for a few pure substances in a chart which is reproduced as Fig. 168.

The Method of Beattie and Bridgman

Beattie† has proposed that the Beattie-Bridgman equation of state for a mixture be obtained by combining the values of the constants from

* *Ind. Eng. Chem.*, Vol. 28 (1936), pp. 212-215.

† *Jl. Am. Chem. Soc.*, Vol. 51 (1929), pp. 19-30.

the equations of state of the pure components. The equation of state of the mixture is

$$p = \frac{RT(1 - \epsilon)}{v^2} (v + B) - \frac{A}{v^2},$$

where $A = A_0(1 - a/v)$, $B = B_0(1 - b/v)$, and $\epsilon = c/vT^3$ where v denotes the volume occupied by the gas per mole of its constituents and R denotes the universal gas constant. Beattie's method of evaluating the constants is given by the following equations:

$$A_0 = [x_a \sqrt{A_{0a}} + x_b \sqrt{A_{0b}} + \dots]^2,$$

$$a = x_a a_a + x_b a_b + \dots,$$

$$B_0 = x_a B_{0a} + x_b B_{0b} + \dots,$$

$$b = x_a b_a + x_b b_b + \dots,$$

$$c = x_a c_a + x_b c_b + \dots,$$

where x_a , x_b , etc., denote the mole fractions of substances a , b , etc., in the mixture, and the symbols A_0 , a , B_0 , b , and c with subscripts a , b , etc., denote the constants in the Beattie-Bridgman equations for pure substances a , b , etc.

The resulting equation of state is generally a good representation of the p - v - T relation for the mixture over the range of conditions for which each pure constituent is fitted by the Beattie-Bridgman equation. That is, the mass of each constituent per unit volume must be less than about one-half the critical density of that constituent.

Determining u , h , and s from the p - v - T Relation

The analytical method employed in the determination of the properties u , h , and s from the p - v - T relation will depend on the form of that relation — whether, for example, it is $v = f(p, t)$ or $p = f(v, t)$ — as well as on the nature of auxiliary information that may be available — whether, for example, it is a set of measured values of the specific heat at constant pressure or of the Joule-Thomson coefficient.

Let us assume for the present that the equation of state is in the form $v = f(p, t)$ and devise a suitable method for evaluating the other properties. The same method will serve if the p - v - T relation is in graphic rather than algebraic form.

The Maxwell relation [193c] gives the partial derivative of the entropy with respect to one of the independent variables in terms of the partial derivative of the volume with respect to the other:

$$\left(\frac{\partial s}{\partial p}\right)_T = - \left(\frac{\partial v}{\partial T}\right)_p \quad [193c]$$

Presumably, the right-hand member of this equation can be evaluated for all states. If it is evaluated for all states at a given temperature we can by integration obtain the change in entropy at that temperature between any two values of the pressure:

$$(s_2 - s_1)_{T=\text{const.}} = \left\{ \int_{p_1}^{p_2} \left(\frac{\partial s}{\partial p} \right)_T dp \right\}_{T=\text{const.}} = - \left\{ \int_{p_1}^{p_2} \left(\frac{\partial v}{\partial T} \right)_p dp \right\}_{T=\text{const.}} \quad [213]$$

Suppose now that the integration is from some line of states of reference along which the entropy is known for different temperatures. This line may be a single line of constant pressure, or the line of saturated vapor states, or any other continuous line. Then we get for the entropy s at the pressure p and the temperature T the expression

$$= - \left\{ \int_x^p \left(\frac{\partial v}{\partial T} \right)_p dp \right\}_{T=\text{const.}} + \phi,$$

where x denotes the pressure and ϕ the entropy on the line of reference at temperature T . The quantities x and ϕ are functions of temperature only. They depend upon the nature of the substance and the course of the line of reference.

A corresponding expression for enthalpy can be deduced as follows: The familiar relation for the pure substance

$$du = T ds - p dv$$

may be readily transformed into the equation

$$dh = T ds + v dp.$$

This is general and may, therefore, be applied to an infinitesimal process at constant temperature. If the resulting equation is divided through by the change in pressure, we get

$$\left(\frac{\partial h}{\partial p} \right)_T = T \left(\frac{\partial s}{\partial p} \right)_T + v.$$

By [193c] we may substitute a volume derivative for the entropy derivative and get

$$\left(\frac{\partial h}{\partial p} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_p. \quad [214]$$

It is easy to convert this into the shorter and more convenient form

$$\left(\frac{\partial h}{\partial p} \right)_T = \left[\frac{\partial (v\tau)}{\partial \tau} \right]_p, \quad [215]$$

where τ denotes the reciprocal of the absolute temperature. The

expression for the enthalpy now becomes

$$h = \left\{ \int_y^p \left[\frac{\partial(v\tau)}{\partial\tau} \right]_p dp \right\}_{T=\text{const.}} + F, \quad [216]$$

where y denotes the pressure and F the enthalpy on a line of reference at temperature T , and both are, therefore, functions of the temperature only.

To complete the expressions for the entropy and the enthalpy it is necessary to know how these quantities vary with change in temperature along their lines of reference. This information the p - v - T relation will not provide. Therefore, supplementary data must be employed.

Suppose, for example, that values of the specific heat at constant pressure are known for all temperatures at one pressure p_1 . Then, if we let

$$x = p_1 = y,$$

we have by the definition of the specific heat at constant pressure (namely, $c_p = [\partial h / \partial T]_p$)

$$F = \int_{T_1}^T c_p dT + h',$$

where h' denotes the arbitrary value of the enthalpy at the reference state p_1, T_1 . Moreover, since

$$c_p = T \left(\frac{\partial s}{\partial T} \right)_p \quad [196]$$

it follows that

$$\phi = \int_{T_1}^T \frac{c_p}{T} dT + s',$$

where s' denotes the arbitrary value of the entropy at the reference state p_1, T_1 . The complete expressions are, therefore,

$$= - \left\{ \int_{p_1}^p \left(\frac{\partial v}{\partial T} \right)_p dp \right\}_{T=\text{const.}} + \int_{T_1}^T \frac{c_p}{T} dT + s' \quad [217]$$

$$= \left\{ \int_{p_1}^p \left[\frac{\partial(v\tau)}{\partial\tau} \right] dp \right\}_{T=\text{const.}} + \int_{T_1}^T c_p dT + h'. \quad [218]$$

An equation of state may not be simple enough to permit the first term in the right-hand member of [217] and that of [218] to be evaluated in algebraic form. But the existence of an equation of state implies that curves of constant pressure can be plotted on a t - v diagram, and from the slopes of such curves the derivatives in [217] and [218] may be evaluated for as many states as desired. The integrations indicated in

[217] and [218] can then be carried out graphically or otherwise. It is apparent that an equation of state is not necessary if a complete μ - p chart is available.

If the h - p - T relation is known from a development of the sort just described, the internal energy can readily be evaluated with the aid of the p - v - T relation. For a given pressure and temperature it is only necessary to evaluate h and v and to compute u from the relation

$$u = h - pv.$$

Since the expressions [217] and [218] involve the slopes of lines of constant pressure on a μ - t chart, the values of s and h found from them are likely to be more gravely affected by errors in the shapes of those lines than by errors in their position. It is conceivable that a chart might represent the p - v - T relation with fair precision and yet be utterly inadequate for evaluating the derivatives in [217] and [218]. This is probably true of most charts that are derived from generalized p - v - T data.

Other Sources of Supplementary Data

Measurements of the specific heat at constant pressure are not the only source of data supplementary to the p - v - T relation. In fact, virtually any measurements that give values of u , h , s , or any of their derivatives would be equally useful. For example, if Joule-Thomson coefficients are known they may be employed by substituting for c_p in [217] and [218] its equivalent $\{-[\partial(v\tau)/\partial\tau]_p/\mu_J\}$, where μ_J denotes the Joule-Thomson coefficient.

An important source of supplementary data may be found in the development of quantum mechanics and the science of interpreting band spectra. The spectrum of the vapor in question is obtained from a spectrograph, and the positions of the lines of the spectrum are measured to determine the corresponding wave lengths. From these can be found the internal energy of the vapor for those states in which the molecules composing it are so far apart as not to influence one another's behavior. Such states are found at vanishingly small pressures.

Since for any gas at zero pressure we may write

$$pv = RT, \tag{18}$$

and from this it follows that the internal energy is independent of the volume (page 98), the specific heat at constant volume $c_{v\infty}$ can be found from the u - T relation. The specific heat at constant pressure for zero pressure c_{p0} is then given by

$$c_{p0} = c_{v\infty} + R$$

in accordance with [22].

In terms of c_{p0} the expression [218] for the enthalpy becomes

$$h = \int_{p=0} \left[\frac{\partial(v\tau)}{\partial\tau} \right]_p dp \Big|_{T=\text{const.}} + \int_{T_1} c_{p0} dT + h', \quad [219]$$

where T_1 and h' are arbitrary quantities. A similar application of the expression for the entropy [217] results in infinite magnitudes for the first and third terms in the right-hand member. It is better to obtain values of h at a finite pressure p_1 from [218] and use these to evaluate the second term of [217].

Another device which permits the direct use of c_{p0} in the expression for entropy involves a quantity D which is defined by the equation

$$D = v - \frac{RT}{p}.$$

The expression for entropy now becomes

$$s = -R \ln p - \left\{ \int_{p=0}^p \left(\frac{\partial D}{\partial T} \right)_p dp \right\}_{T=\text{const.}} + \int_{T_1}^T \frac{c_{p0}}{T} dT + s'. \quad [220]$$

Here terms of infinite magnitude are avoided by including a term $R \ln 0$ in the arbitrary constant s' .

Development of the Equation of State

If an equation of state is of the form

$$v = f(p, t)$$

the corresponding values of enthalpy and entropy may be found from [219] and [220] or from similar equations designed to employ different supplementary data. An example of a complete development of this sort will be found on pages 15 to 20 of *Thermodynamic Properties of Steam*.*

Any equation of the form

$$p = f(v, T)$$

must either be changed to the other form or developed in a different fashion. For the latter purpose we would substitute the Maxwell relation

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v \quad [192c]$$

* Keenan and Keyes, Wiley, 1936:

for [193c], and the relation

$$\left(\frac{\partial u}{\partial v}\right)_T = - \left[\frac{\partial(p\tau)}{\partial \tau} \right]_v \quad [221]$$

for the analogous one used above.

The expression corresponding to [219] is now

$$u = - \left\{ \int_{v=\infty}^v \left[\frac{\partial(p\tau)}{\partial \tau} \right]_v dv \right\}_{T=\text{const.}} + \int_{T_1}^T c_{v\infty} dT + u'', \quad [219a]$$

where u'' is an arbitrary constant. If we define a quantity D' through the equation

$$p = \frac{RT}{v} + D',$$

then the expression corresponding to [220] is

$$s = R \ln v + \left(\frac{\partial D'}{\partial T} \right)_v \int_{v=\infty}^v dv \Big|_{T=\text{const.}} + \int_{T_1}^T \frac{c_{v\infty}}{T} dT + s'', \quad [220a]$$

where s'' is an arbitrary constant.

If we apply these expressions to the equation of van der Waals we get

$$u = - \frac{a}{v} + \int_{T_1}^T c_{v\infty} dT + u' \quad [222]$$

and

$$s = R \ln (v - b) + \int_{T_1}^T \frac{c_{v\infty}}{T} dT + s''. \quad [223]$$

If we apply them to the equation of Beattie and Bridgman we get

$$u = \frac{A_0}{v} \left(\frac{a}{2v} - 1 \right) - \frac{3Rc}{vT^2} \left(1 + \frac{B_0}{2v} - \frac{B_0b}{3v^2} \right) + \int_{T_1}^T c_{v\infty} dT + u'' \quad [224]$$

and

$$s = R \ln v - \frac{RB_0}{v} \left(1 - \frac{b}{2v} \right) - \frac{2Rc}{vT^3} \left(1 + \frac{B_0}{2v} - \frac{B_0b}{3v^2} \right) + \int_{T_1}^T \frac{c_{v\infty}}{T} dT + s''. \quad [225]$$

Development of Specific-Heat and Joule-Thomson Data

The methods described above for determining u , h , and s from the p - v - T relation can be reversed to determine the p - v - T relation from experimental data relating to the other properties.

Davis* has devised an ingenious and graphic method of developing data on the Joule-Thomson effect to give the properties v , h , u , and s as functions of p and T .

Hausen† formulated the extensive measurements of the specific heat of steam, made by Knoblauch and his colleagues as a function of p and T . He then devised a means of developing from this formulation an equation of state. This development formed the basis of a set of *Steam Tables*.

The Fundamental Equation

If we review the development of the p - v - T relation as outlined above we find that in each instance the quantities u , h , and s were determined from values of their partial derivatives which were implicit in the p - v - T relation. Thus, we obtained values of the constant-temperature coefficient $(\partial h/\partial p)_T$ by evaluating $[\partial(v\tau)/\partial\tau]_p$ and values of $(\partial s/\partial p)_T$ by evaluating $(\partial v/\partial T)_p$.

From these quantities we obtained expressions for h and s which include unknown functions, F and ϕ , of the temperature:

$$h = \int_v^p \left[\frac{\partial(v\tau)}{\partial\tau} \right]_x dp + F \quad [226]$$

$$s = - \int_x^p \left(\frac{\partial v}{\partial T} \right) dp + \phi. \quad [227]$$

In order to evaluate F and ϕ it was necessary to introduce information supplementary to the p - v - T relation. Since this analytical complication arises because h and s must be found through integration, it is desirable to start the analysis with some substitute for the p - v - T relation which is of such a nature that all other properties can be found through differentiation. Relations of this nature were called *characteristic functions* by Massieu.

For example, the internal energy may be considered as a function of volume and entropy,

$$u = f(v, s). \quad [228]$$

From the First and Second Laws we may write

$$du = T ds - p dv. \quad [15]$$

It follows that

$$T = \left(\frac{\partial u}{\partial s} \right)_v$$

* H. N. Davis, *Mechanical Engineering*, Vol. 46 (1924), p. 85.

† *Tabellen u. Diagramme f. Wasserdampf*, Knoblauch et al., R. Oldenbourg (1932), p. 13.

and

$$p = - \left(\frac{\partial u}{\partial v} \right)_s.$$

The other thermodynamic properties may be expressed in terms of these:

$$h = u - v \left(\frac{\partial u}{\partial v} \right)_s,$$

$$\psi = u - s \left(\frac{\partial u}{\partial s} \right)_v,$$

and

$$\zeta = u - v \left(\frac{\partial u}{\partial v} \right)_s - s \left(\frac{\partial u}{\partial s} \right)_v.$$

It can be seen that the characteristic function embraces a complete statement of all the thermodynamic properties.*

Other characteristic functions are

$$h = f(p, s),$$

$$\psi = f(v, T), \quad [229]$$

and

$$\zeta = f(p, T).$$

It is never possible to begin the formulation of properties of a substance in terms of any one of the four characteristic functions because in none of them are all three properties conveniently measurable. Therefore, it is necessary to begin with one of the less complete formulations relating quantities more commonly measured. Nevertheless, the characteristic function serves a useful purpose as an indicator of the completeness of a formulation. When a formulation has been developed to a point where any one of the characteristic functions can be determined, it is complete.

PROBLEMS

1. Plot on the same μ - p_R chart the saturation line for ammonia and that for steam (and any other substances for which you have data available) and that taken from Weber's generalized chart (Fig. 166).

* It is easy to show that $v = f(p, T)$ is not a characteristic function. From [193a],

$$v = \left(\frac{\partial \zeta}{\partial p} \right)_T.$$

Therefore

$$\left(\frac{\partial \zeta}{\partial p} \right)_T = f(p, T),$$

and ζ cannot be expressed without including an unknown function of T .

2. From generalized p - v - T relations and data from Table VIII find values for the density of propane in the following states. (Use the most appropriate method in each instance.)

STATE		a	b	c	d
p	lb/sq in. abs	5	300	600	1000
t	F	700	250	100	400

3. (a) Plot on a p - v diagram the isotherm for propane at 120 F between 100 and 250 lb/sq in. abs.

(b) How much work would be done by 1 lb of propane expanding reversibly and isothermally from 250 to 100 lb/sq in. abs at 120 F?

(c) How much shaft work per pound of propane must be supplied to a reversible isothermal compressor that compresses propane in steady flow at 120 F from 100 to 250 lb/sq in. abs?

4. (a) Find values for the constants of the van der Waals equation corresponding to the critical pressure and temperature of steam. Plot the critical isotherm from this equation and that from the *Steam Tables* on a μ - p chart.

(b) Plot the isotherms of the equation of state and of the *Steam Tables* for 500 F. Locate the saturation states corresponding to the equation.

5. Using the constants given in Table IX for the Beattie-Bridgman equation compute the isotherm for 150 F for ammonia. Plot it on a μ - p chart, and plot the corresponding curve from the ammonia tables of the Bureau of Standards.

6. Plot on one diagram p_R against T_R for saturated ammonia and saturated steam.

7. Using the *Steam Tables* and critical data on ammonia from Table VIII find from the Law of Corresponding States a value for the specific volume of ammonia at 100 lb/sq in. abs and 200 F. Compare this figure with that given in the ammonia tables of the Bureau of Standards.

8. Assume that the Gibbs-Dalton Law holds for mixtures of a group of gases, and that the equation of state of each gas is of the virial form

$$p_1 = \frac{RT}{v_1} + \frac{\alpha_1}{v_1^2} + \frac{\beta_1}{v_1^3} + \cdots,$$

where v denotes the molal volume, and subscript 1 refers to gas 1. Find expressions for the constants in the equation of state of the mixture

$$p = \frac{RT}{v} + \frac{\alpha}{v^2} + \frac{\beta}{v^3} + \cdots,$$

in terms of the constants in the equations of the constituents.

9. Demonstrate the following relations:

$$(a) \quad v - T \left(\frac{\partial v}{\partial T} \right)_p = \left[\frac{\partial(v\tau)}{\partial \tau} \right]_z$$

$$(b) \quad c_p = T \left(\frac{\partial s}{\partial T} \right)_p,$$

$$(c) \quad c_p = - \frac{1}{\mu_J} \left[\frac{\partial(v\tau)}{\partial \tau} \right]_p,$$

where μ_J denotes the Joule-Thomson coefficient.

$$(d) \quad = -R \ln p - \int_0^p \left(\frac{\partial D}{\partial T} \right)_p dp + \int_{T_1}^T \frac{c_{p0}}{T} dT + s,$$

where $D = v - RT/p$.

$$(e) \quad \left(\frac{\partial u}{\partial v} \right)_T = - \left[\frac{\partial(p\tau)}{\partial \tau} \right]_v,$$

$$(f) \quad s = R \ln v + \int_{\infty}^v \left(\frac{\partial D'}{\partial T} \right)_v dv + \int_{T_1}^T \frac{c_{v\infty}}{T} dT + s''$$

where $D' = p - RT/v$.

(g) The expressions for u and s , [222] and [223], corresponding to the van der Waals equation.

(h) Those, [224] and [225], corresponding to the Beattie-Bridgman equation.

10. (a) Show that the upper and lower envelopes of the μ - p chart correspond to the inversion line of the Joule-Thomson coefficient.

(b) Derive an expression for the inversion line of van der Waals' equation in terms of reduced volume and temperature. Plot it on a T_R - p_R diagram and on a p_R - v_R diagram, and show the critical point for comparison. Note that the inversion line crosses the line of zero pressure at a finite volume. What is the significance of this crossing?

11. (a) Using van der Waals' equation as a guide, estimate the temperature of inversion at zero pressure for steam and for hydrogen. Note that steam has a positive and hydrogen a negative Joule-Thomson coefficient at room temperature.

(b) Find a value for the temperature of inversion at zero pressure for steam from equation [13], page 15, of Keenan and Keyes. (Note that for very low pressures [13] reduces to $v = RT/p + B_0$.)

(c) Using van der Waals' equation as a guide estimate the temperature of inversion for liquid water. Find the temperature of inversion from Table 4 of Keenan and Keyes.

12. Find expressions for the algebraic portions of the expressions for $(h-h_f)$ and $(s-s_f)$ given on page 20 of Keenan and Keyes.

13. Find an expression for the volume at a state p, t in terms of the quantities in equation [19] of Keenan and Keyes and the volume for an isometric for which the p - t relation is known.

14. Derive a fundamental equation for a perfect gas.

SYMBOLS

A_0, B_0, a, b, c	constants Beattie-Bridgman equation
c_p	specific heat at constant pressure
c_v	specific heat at constant volume
D	$(v - RT/p)$
D'	$(p - RT/v)$,
F	function of temperature
h	enthalpy per unit mass
p	pressure

R	gas constant
R	universal gas constant
s	entropy per unit mass
s''	arbitrary constant
T	absolute temperature
u	internal energy of a unit system in the absence of motion, gravity, etc.
u''	arbitrary constant
v	specific volume
v	volume per mole
V	volume
x	function of temperature
$x_a, x_b, \text{etc.}$	mole fractions of constituents $a, b, \text{etc.}$, in mixture
y	function of temperature

GREEK LETTERS

α	function of temperature only
ϵ	(c/vT^3) Beattie-Bridgman equation
ϕ	a function, slope of an isometric of a mixture
τ	reciprocal of absolute temperature
μ	pv/RT
μ_J	Joule-Thomson coefficient

SUBSCRIPTS

c	critical point
R	ratio of indicated property to the property at the critical state

SUPERScript

a number greater than 1

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CHAPTER XXI

THERMODYNAMIC TEMPERATURE AND THE INTERNATIONAL SCALE OF TEMPERATURE

The Thermodynamic Scale of Temperature

The ratio of two temperatures on the Kelvin scale of temperature (and on its counterpart the absolute Fahrenheit scale) is defined in Corollary 3 of the Second Law as

$$\frac{T_1}{T_2} = \frac{q_1}{q_2} \quad [11]$$

where q_1 and q_2 are respectively the heat received and the heat rejected by a reversible engine working between the temperatures T_1 and T_2 .

Now a reversible engine is a limiting type which actual engines can be made to approach but never to equal in performance. Therefore, temperatures on the absolute scale cannot be measured in so direct a fashion.

However, any of the relationships between temperature and other measurable properties deduced from the First and Second Laws afford means of identifying the value on the Kelvin scale for a given level of temperature. The Clapeyron relation [202] is an example. Using h_{fg} and v_{fg} for the change in enthalpy and volume, respectively, during vaporization we may state the Clapeyron relation in the form

$$\frac{dT}{T} = \frac{v_{fg}}{h_{fg}} dp. \quad [230]$$

If for any substance the values of h_{fg} and v_{fg} are measured over a range of saturation pressures, the ratio of the two temperatures on the Kelvin scale lying within the range of the measurements can be found from the definite integral of [230]; that is

$$\ln \frac{T_2}{T_1} = \int_{p_1}^{p_2} \frac{v_{fg}}{h_{fg}} dp.$$

The present state of our knowledge of the properties of water would permit us to obtain temperatures between 300 and 600 on the Kelvin scale to fair precision by this means. However, methods are available

which are more precise because they involve fewer and simpler measurements.

The basis for the most precise methods employed in determining temperatures on the thermodynamic scale is the fact that the isotherms of a pure substance on a chart of $p\nu/RT$ against p converge on the ordinate 1 with finite slope and decreasing curvature as p approaches zero. In general the equation of state of a pure substance may be of the form

$$\frac{p\nu}{RT} = 1 + \alpha_1 p + \sum \alpha_i p^i, \quad [209]$$

where each α is a pure temperature function and the exponents i are all greater than unity. Therefore, at low pressures it will simplify to

$$\frac{p\nu}{RT} = 1 + \alpha_1 p. * \quad [231]$$

This is the linear relation that an isotherm approaches as p approaches zero.

The ratio between two values of temperature on the thermodynamic scale corresponding to any two reproducible levels of temperature (say the temperature of boiling water and that of melting ice, both under a pressure of 1 standard atmosphere) can be found by measuring the volume of any vapor or mixture of vapors at several low pressures at each level of temperature. The product of pressure and volume

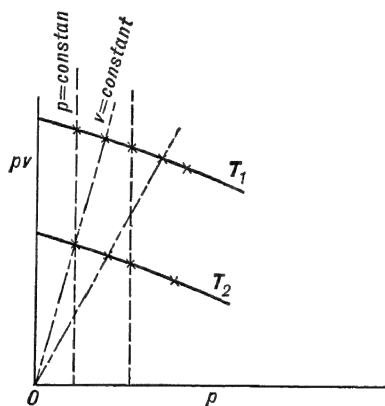


FIG. 169

may be plotted against pressure as in Fig. 169 and the resulting curves extrapolated to zero pressure. Then from [231]

$$\frac{T_1}{T_2} = \lim_{p \rightarrow 0} \left[\frac{(p\nu)_1}{(p\nu)_2} \right]. \quad [232]$$

* Beattie has shown that in order to arrive at [231] it is only necessary to assume that at low pressures the internal energy of a gas approaches a function of the temperature in the manner given by

$$u = f(T) + \xi p,$$

where $f(T)$ and ξ are pure temperature functions. (*Physical Review*, Vol. 36 (1930), pp. 132-145.)

In precise determinations of temperatures on the thermodynamic scale more refined methods of extrapolation are used. It should be noted that the experimental points indicated in Fig. 169 will not fall on straight lines unless all measurements are carried out at such low pressures that the terms having higher exponents than 1 in [209] are negligible.

A gas thermometer is an apparatus for making measurements of p , v , and T at low pressures. Two types, the constant-pressure thermometer and the constant-volume thermometer, are commonly employed. In the constant-pressure thermometer the volume occupied by a fixed mass of vapor is measured at the different levels of temperature at some one pressure. The measurements (values from which would lie on the vertical lines of Fig. 169) are repeated for different pressures over a sufficient range to guide the extrapolation to zero pressure. In the constant-volume thermometer the pressure of a fixed mass of vapor in a container of invariable volume is measured at the different levels of temperature. The mass confined is changed, and the measurements (values from which would lie on the radiating lines of Fig. 169) are repeated until enough data are obtained to guide the extrapolation.

In gas thermometry any vapor can be used but certain vapors are preferred. Among the characteristics of a preferred vapor are (a) a small value of α_1 , (b) negligible adsorption on the container walls, (c) a low rate of diffusion through the container walls. Of these, (c) indicates a vapor of high molecular weight and (b) a vapor with low critical temperature. If (a) is satisfied, then

$$\frac{T_1}{T_2} \cong \frac{(pv)_1}{(pv)_2}$$

for any low pressure.

The definition of the Kelvin scale specifies that the interval of temperature between that level at which ice and air-saturated water are in equilibrium under a pressure of 1 standard atmosphere and that at which liquid water and its vapor are in equilibrium under the same pressure shall be 100 degrees. Measurements made with gas thermometers at these levels of temperature give the value 1.36609 ± 0.00004 for the ratio of the two temperatures. Combining this value with the prescribed interval of 100 degrees we get for the lower level of temperature 273.16 ± 0.03 and for the higher level 373.16 ± 0.03 .

The absolute Fahrenheit scale is defined in the same way as the Kelvin scale except that the interval between the same prescribed levels of temperature is 180 degrees. The corresponding magnitudes of the prescribed levels are 491.69 ± 0.05 and 671.69 ± 0.05 .

The International Scale of Temperature

Because of the relative complexity of the gas thermometer and the elaborate technique necessary to obtain precise results it is used only as an ultimate standard. For the calibration of thermometers used in scientific and engineering practice it is desirable to have a simpler instrument which, by virtue of its simplicity, will have a higher degree of reproducibility of result than the gas thermometer in its present state of development. Such an instrument can be established as a standard of comparison, and its indications can be converted to thermodynamic temperatures by means of an equation which states, so far as it has been determined, the relationship between the two. In this fashion all calibrated thermometers can be caused to indicate temperatures corresponding as nearly as possible to the correct temperature on the absolute scale.

In 1927 the Seventh General Conference of Weights and Measures representing 31 nations adopted unanimously a temperature standard proposed by the national laboratories of the United States, Great Britain, and Germany. Its definition involves: first, the assignment of the most probable values on the absolute scale, in view of existing data, to certain reproducible levels of temperature (melting points, condensation points, etc.); second, a description of an instrument as an indicator; and third, an interpolation formula relating the change in indication of the instrument and the change in thermodynamic temperature, as closely as was possible at that time, between either of a pair of adjacent fixed points and any intermediate level of temperature.

The following is quoted from the report by Burgess on the decisions of the international conference:*

It is to be understood that this proposal does not purport to replace the absolute temperature scale which it is recommended should be adopted, on principle, by the International Conference on Weights and Measures. It is intended merely to represent this scale in a practical manner with sufficient accuracy to serve the everyday needs of the laboratories for the purpose of industrial certifications, and is to be regarded as susceptible of revision and amendment as improved and more accurate methods of measurement are evolved.

It is anticipated that this scale will shortly be adopted by the three laboratories for the purposes indicated, and the attached draft is presented to the conference for consideration, with the recommendation that it should be officially adopted, with such amendments, if any, as may be agreed on, as the best practical realization at the present time of the ideal thermometric scale.

* *Bureau of Standards Journal of Research*, Vol. 1 (1928), pp. 636-637.

PART I. DEFINITION OF THE INTERNATIONAL TEMPERATURE SCALE

1. The thermodynamic Centigrade scale,* on which the temperature of melting ice, and the temperature of condensing water vapor, both under the pressure of 1 standard atmosphere, are numbered 0 degrees and 100 degrees, respectively, is recognized as the fundamental scale to which all temperature measurements should ultimately be referable.

2. The experimental difficulties incident to the practical realization of the thermodynamic scale have made it expedient to adopt for international use a practical scale designated as the international temperature scale. This scale conforms with the thermodynamic scale as closely as is possible with present knowledge, and is designed to be definite, conveniently and accurately reproducible, and to provide means for uniquely determining any temperature within the range of the scale, thus promoting uniformity in numerical statements of temperature.

3. Temperatures on the international scale will ordinarily be designated as "°C," but may be designated as "°C (Int.)" if it is desired to emphasize the fact that this scale is being used.

4. The international temperature scale is based upon a number of fixed and reproducible equilibrium temperatures to which numerical values are assigned, and upon the indications of interpolation instruments calibrated according to a specified procedure at the fixed temperatures.

5. The basic fixed points and the numerical values assigned to them for the pressure of 1 standard atmosphere are given in the following table, together with formulas which represent the temperature (t_p) as a function of vapor pressure (p) over the range 680 to 780 mm of mercury.

6. Basic fixed points of the international temperature scale:

(a) Temperature of equilibrium between liquid and gaseous oxygen at C
the pressure of 1 standard atmosphere (oxygen point) -182.97

$$t_p = t_{760} + 0.0126(p - 760) - 0.0000065(p - 760)^2.$$

(b) Temperature of equilibrium between ice and air-saturated water
at normal atmospheric pressure (ice point) 0.000

(c) Temperature of equilibrium between liquid water and its vapor at
the pressure of 1 standard atmosphere (steam point) 100.000

$$t_p = t_{760} + 0.0367(p - 760) - 0.000023(p - 760)^2.$$

* A temperature on the thermodynamic Centigrade scale is less than the corresponding temperature on the Kelvin (absolute Centigrade) scale by the temperature of the ice point on the Kelvin scale. Thus

$$t = T - T_0,$$

where t denotes the temperature on the thermodynamic Centigrade scale, T the temperature on the Kelvin scale, and T_0 the temperature of the ice point on the Kelvin scale.

(d) Temperature of equilibrium between liquid sulphur and its vapor at the pressure of 1 standard atmosphere (sulphur point) 444.60

$$t_p = t_{760} + 0.0909(p - 760) - 0.000048(p - 760)^2.$$

(e) Temperature of equilibrium between solid silver and liquid silver at normal atmospheric pressure (silver point) 960.5

(f) Temperature of equilibrium between solid gold and liquid gold at normal atmospheric pressure (gold point) 1063

Standard atmospheric pressure is defined as the pressure due to a column of mercury 760 mm high, having a mass of 13.5951 g/cm³, subject to a gravitational acceleration of 980.665 cm/sec², and is equal to 1,013,250 dynes/cm².

It is an essential feature of a practical scale of temperature that definite numerical values shall be assigned to such fixed points as are chosen. It should be noted, however, that the last decimal place given for each of the values in the table is significant only as regards the degree of reproducibility of that fixed point on the international temperature scale. It is not to be understood that the values are necessarily known on the thermodynamic Centigrade scale to the corresponding degree of accuracy.

7. The means available for interpolation lead to a division of the scale into four parts.

(a) From the ice point to 660 C the temperature t is deduced from the resistance R_t of a standard platinum resistance thermometer by means of the formula

$$R_t = R_0 (1 + At + Bt^2).$$

The constants R_0 , A , and B of this formula are to be determined by calibration at the ice, steam, and sulphur points, respectively.

The purity and physical condition of the platinum of which the thermometer is made should be such that the ratio R_t/R_0 shall not be less than 1.390 for $t = 100$ degrees and 2.645 for $t = 444.6$ degrees.

(b) From -190 degrees to the ice point, the temperature t is deduced from the resistance R_t of a standard platinum resistance thermometer by means of the formula

$$R_t = R_0 (1 + At + Bt^2 + C[t - 100]t^3).$$

The constants R_0 , A , and B are to be determined as specified above, and the additional constant C is determined by calibration at the oxygen point.

The standard thermometer for use below 0 C must, in addition, have a ratio R_t/R_0 less than 0.250 for $t = -183$ degrees.

(c) From 660 C to the gold point, the temperature t is deduced from the electromotive force e of a standard platinum vs. platinum-rhodium thermocouple, one junction of which is kept at a constant temperature of 0 C while the other is at the temperature t defined by the formula

$$e = a + bt + ct^2.$$

The constants a , b , and c are to be determined by calibration at the freezing point of antimony, and at the silver and gold points.

(d) Above the gold point the temperature t is determined by means of the ratio of the intensity J_2 of monochromatic visible radiation of wave length λ cm, emitted by a black body at the temperature t_2 , to the intensity J_1 of radiation of the same wave length emitted by a black body at the gold point, by means of the formula

$$\log_e \frac{J_2}{J_1} = \frac{c_2}{\lambda} \left(\frac{1}{1336} - \frac{1}{(t + 273)} \right).$$

The constant c_2 is taken as 1.432 cm degrees. The equation is valid if $\lambda(t + 273)$ is less than 0.3 cm degrees.

Temperatures on the absolute thermodynamic scale are best known in the range covered by the platinum resistance thermometer and the quadratic formula (0 – 660 C). The most recent measurements with a gas thermometer of temperatures on the thermodynamic scale are shown

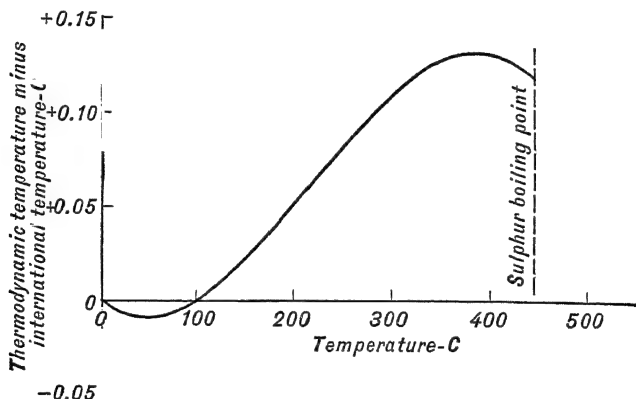


FIG. 170. Departure of the Thermodynamic Scale from the International Scale
Based on measured values made available through the courtesy of Professor James A. Beattie.

in Fig. 170 as departures from temperatures on the international scale. They indicate that the temperature assigned to the boiling point of sulphur on the international scale is lower than the temperature on the thermodynamic scale by 0.12 C. All other differences between the ice point and the boiling point of sulphur are less than 0.15 C. The maximum departure from unity of the derivative of values on one scale with respect to values on the other appears to be less than 1 part in 2500 in this range.* Therefore no distinction need be made, except in the most

* The importance of this derivative in thermodynamic relations may be seen from the equation

$$\left(\frac{\partial x}{\partial T} \right)_y = \left(\frac{\partial x}{\partial t_i} \right)_y \cdot \frac{dt_i}{dT},$$

where x and y are any pair of properties of a system and t_i and T are respectively the international and the absolute temperatures.

precise scientific work, between the international Centigrade scale and the thermodynamic Centigrade scale.

SYMBOLS

c_2	a constant
e	electromotive force
h	enthalpy per unit mass
J	intensity of radiation
p	pressure
q	a positive number representing a quantity of heat
R	gas constant
R_0	a constant
R_t	electrical resistance
t	temperature on thermodynamic Centigrade scale
t_i	international temperature
T	absolute temperature
T_0	temperature of ice point on Kelvin scale
u	internal energy of a unit system in the absence of motion, gravity, etc.
v	specific volume

GREEK LETTERS

α	a function of temperature
ζ	a function of temperature

SUBSCRIPTS

fg	change between saturated liquid and saturated vapor states
p	constant pressure
t	constant temperature

SUPERScript

i	a number greater than 1
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CHAPTER XXII

BINARY MIXTURES

Equilibrium between Liquid and Vapor Phases

When one component of a mixture is soluble in all proportions in the liquid of the other component then the mixture may exist either as a gas or as a liquid. Let us describe a chart for which the ordinate is temperature and the abscissa is x_1 , the proportion of substance 1 in a mixture of substances 0 and 1: thus

$$x_1 = \frac{m_1}{m},$$

where m_1 is the mass of component 1 in a mass m of the mixture.

For any given pressure of the mixture there is a temperature t_1 (Fig. 171), the boiling point of the pure liquid 1, for which a mixture of composition $x_1 = 1$ will boil. Moreover, for the same pressure there is

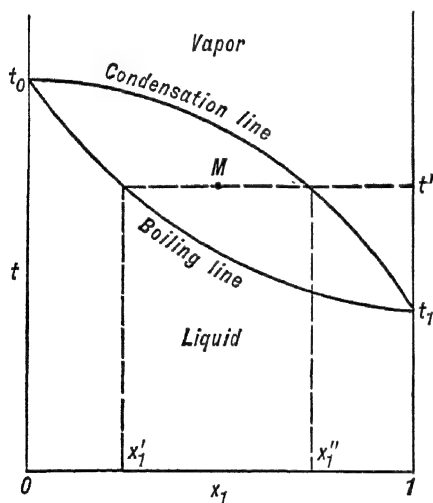


FIG. 171. Temperature-Composition Chart for a Binary Mixture

a different temperature t_0 , the boiling point of pure liquid 0, for which a mixture of composition $x_1 = 0$ will boil. Thus the two points on the chart $x_1 = 0, t = t_0$, and $x_1 = 1, t = t_1$, each indicate not only the temperature of equilibrium between liquid and vapor but also the composition of the liquid and that of the vapor in equilibrium with it.

If we choose a liquid of intermediate composition x'_1 we find that it begins to boil at a temperature t' which is in general different from either t_0 or t_1 . The vapor given off by such a liquid is likely, however, to be richer in the more volatile component of the liquid (component 1 in Fig. 171) than is the liquid itself.* That is, at temperature t' the liquid of composition x'_1 will be in equilibrium with a vapor

* Azeotropic mixtures are exceptions. They are treated in Chapter XXVI.

of composition x''_1 . By measuring for each composition of the liquid the composition of vapor that can coexist in equilibrium with it as well as the temperature of equilibrium, data may be obtained corresponding to the curves marked "boiling line" and "condensation line" in Fig. 171. All possible vapor states of mixtures at the assumed pressure are represented by points in the area above the condensation line, and all possible liquid states by points in the area below the boiling line. Between the two lines lie points representing states which include both liquid and vapor phases. The point M , for example, represents a state which comprises liquid of composition x'_1 and vapor of composition x''_1 , both at temperature t' .

When the pressure is altered the positions of the two lines alter with it. If the pressure rises the boiling points of both components increase and the two lines rise, and conversely.*

Rectification

The process of separating a mixture into its components is called *rectification*. A method of partial rectification at constant pressure can be devised as follows: Let a stream of liquid mixture be introduced into a downward-sloping passage at A (Fig. 172), the depth of the stream being less than the depth of the passage. The liquid has a composition x'_1 , and its temperature is the corresponding boiling temperature t' . At the bottom of the passage heat is added to the stream so that vaporization occurs and vapor flows back up the passage counter to the flow of liquid. Heat transfer between vapor and liquid will cause evaporation from the surface of the descending stream of liquid. Now any vapor generated from the incoming liquid will have the composition x''_1 ; that is, it will be richer in component 1 (the more volatile component) than the liquid.

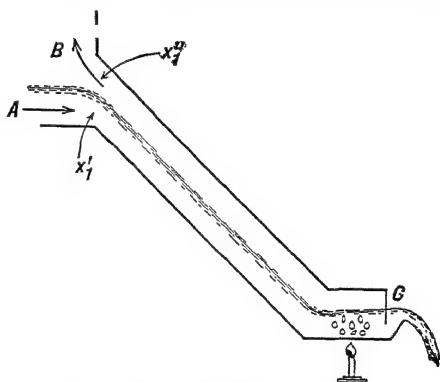


FIG. 172. Partial Rectification

* It should be noted that there are two independent properties — for example, temperature and composition — for a phase of a binary mixture when that phase is in equilibrium with a second phase. On the other hand, there is only one independent property — for example, temperature — for a phase of a pure substance in equilibrium with a second phase. The number of independent phase properties is the value of F in the phase rule, page 478, Chapter XXVI.

Therefore the liquid passing downward will have less and less of component 1 (lower x_1) and will therefore boil at higher and higher temperatures (see Fig. 171). Consequently we may trap off at G a hot liquid from which most of the more volatile component has been driven off. With adequate area of liquid-vapor surface and careful control of the supply of heat it is possible, in the limit, to discharge pure liquid at G . If we assume that the vapor discharged at B is in equilibrium with the entering liquid and that pure liquid is discharged at G we may compute the relative rates of flow at A , B , and G . Thus, the mass flow of component 1 into the apparatus at A equals its mass flow out at B , or

$$x_1' = x_1'' w_B,$$

where w_B is the ratio of mass flow at B to the entering mass flow. Then

$$w_B = \frac{x_1'}{x_1''}$$

and

$$w_G = 1 - \frac{x_1'}{x_1''},$$

where w_G is the ratio of mass flows at G and A . For any lesser flow of pure liquid at G the vapor at B will be richer in component 0, so that

its value of x will be less and its temperature will be higher than the temperature of the incoming liquid. This is a necessary condition for a finite rate of transfer of heat with finite surface, so that the full yield of pure liquid ($1 - x_1'/x_1''$) cannot be realized. The quantity ($1 - x_1'/x_1''$) is the maximum yield of pure liquid, for any greater yield would result in a higher value of x for the vapor and a reversal of the direction of transfer of heat.

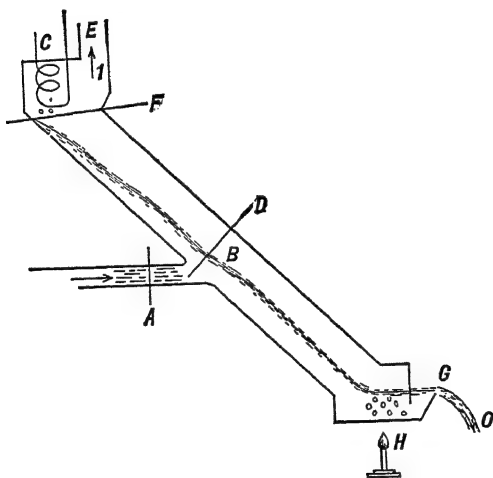


FIG. 173. Complete Rectification

Complete separation can be realized if the device of Fig. 172 is modified as shown

in Fig. 173 by extending the passage upward from the inlet opening and providing at the top a cooling surface C and a gas outlet

E. Now the cold condensate from the cooling surface flows down the passage and causes condensation of vapor and establishes a temperature gradient between the temperature of the inlet and the temperature of the cooling surface. The vapor ascending beyond the inlet level *B* is cooled by the descending liquid and the less volatile component is condensed out of it, so that at the top of the column at a temperature of t_1 it can be in equilibrium with pure liquid of substance 1. Some of this liquid must be formed by condensation and started downward to establish the temperature gradient. The minimum ratio of *reflux* (or returning flow) of condensed liquid at the level *D*, of the entering stream to the mass flow of the entering stream will be realized when the liquid at *D* is identical in composition and state with the liquid entering at *A* and the vapor at *D* is in equilibrium with the liquid there. Let us consider a period of time during which a unit mass of fluid of composition x_1 enters at *A*. During that same period the flow out is x'_1 at *E* and $(1 - x'_1)$ at *G*, because the entire flow entering must be accounted for by the flow of pure components out at *E* and *G*. Accounting for the flow of component 1 across the section *D* and out at *E*, we write

$$w'_D x'_1 + x'_1 = w''_D x''_1,$$

where w'_D denotes the reflux of liquid at *D*, w''_D the flow of vapor past *D*, and x''_1 the composition of the vapor. Accounting similarly for the flow of component 0 across sections *A* and *D* and out at *G*, we write

$$(w'_D + 1)(1 - x'_1) = w''_D(1 - x''_1) + (1 - x'_1).$$

Solving these two equations for the minimum reflux w'_D per unit of fluid entering at *A*, we get

$$w'_D = x'_1 \frac{1 - x''_1}{x''_1 - x'_1}, \quad [233]$$

Any greater reflux will increase the differences in temperature between liquid and vapor and increase the capacity of the rectifier.

The ratio of the flow of condensate from cooler *C* to the inlet flow at *A* is dependent on the properties of the pure component 1 and of the liquid and vapor mixtures at the inlet level. We may apply the energy equation of steady flow to a section *D* immediately above the inlet and to a section *F* immediately below the condenser. Using a single accent to denote the liquid phase and a double accent to denote the vapor phase, we get

$$w'_F h''_F + w'_D h'_D = w'_F h'_F + w''_D h''_D,$$

where w denotes the rate of flow per unit rate of inlet flow at *A*, h

denotes the enthalpy of unit mass of fluid, and the subscripts refer to sections. Using subscript E to denote the vapor leaving the top of the column, we have

$$w_F'' = w_E + w_F'$$

and

$$w_D'' = w_E + w_D'$$

Combining these three equations and solving for the rate of condensation w_F' , we get

$$w_F' = \frac{w_E(h_D'' - h_E) + w_D'(h_D'' - h_D')}{h_E - h_F'} \quad [234]$$

where h_E has been substituted for its equivalent h_F'' . If the liquid and vapor are in equilibrium at F the denominator becomes the latent heat of vaporization L_1 of pure substance 1. Moreover, for equilibrium between liquid and vapor at D , h_D' becomes identical with the enthalpy of unit mass of the entering stream and h_D'' the enthalpy of vapor in equilibrium with it, and the difference between them may be denoted by L_A . Since for complete rectification substance 1 leaves only at E , it follows that

$$w_E = x_1',$$

where x_1' is the proportion of substance 1 in the entering liquid. With these substitutions and with the value given by [233] for w_D' , [234] becomes

$$w_F' = \frac{x_1'}{L_1} \left[(h_A'' - h_E) + L_A \frac{1 - x_1''}{x_1'' - x_1'} \right].$$

The rate of heat transfer to the cooling surface C is, of course,

$$Q_c = w_F' L_1$$

per unit rate of flow entering at A . These values for w_F' and Q_c are the minimum values for complete rectification. By analogous methods similar expressions can be found for the minimum vaporization at the bottom of the column and for the minimum transfer of heat to the column.

The Polar Diagram

The corresponding states of the liquid and vapor passing any section of a rectifying column are related through a polar diagram on an enthalpy-composition chart. This relation can be derived by applying the energy equation of steady flow to one end of the column. Let w_e

denote the mass flow of vapor out at E (Fig. 174), w' the flow of liquid and w'' the flow of vapor across section S , and Q_c the flow of heat out of the system at the top of the column, all for the same period of time. Then

$$w' + w_e = w''.$$

Denoting enthalpies and compositions in a manner analogous to that for flows, we get for the flow of one component

$$x'w' + x_e w_e = x''w'',$$

and for the energy equation

$$w'h' + w_e h_e + Q_c = w''h''.$$

Combining these three equations we get

$$h' + \frac{x_e - x'}{x' - x''} (h' - h'') = h_e + q, \quad [235]$$

where q denotes the heat transferred per unit of mass discharged at E .

For all sections S the value of the right-hand member of [235] will be the same. If we select a section at which the liquid has the composition

x' and the enthalpy h' , consistent with the properties of a saturated liquid, then [235] yields a linear relation between the composition x'' and the enthalpy h'' of the vapor at that section. If this relation is plotted on an enthalpy-composition chart (Fig. 175) it will be a straight line which will intersect the curves of saturated liquid and saturated vapor at the states corresponding to section S .

If the straight line is extended until it crosses the abscissa x_e , it will be at the ordinate $(h_e + q)$ at the intersection.

There will be similar straight lines for all sections S , and all these must cross the abscissa x_e at the ordinate $(h_e + q)$, that is, at a single point P (Fig. 175).

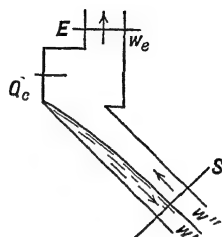


FIG. 174

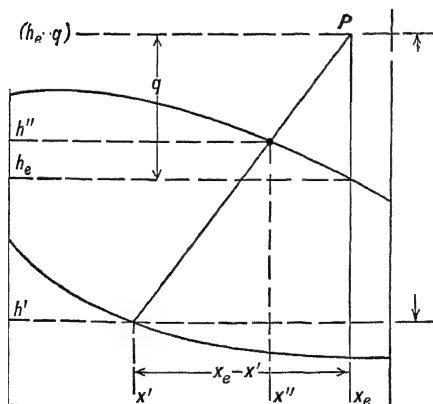


FIG. 175. The Polar Diagram

In Fig. 176 the line PR denotes a section part way down the column. From the lines of constant temperature shown on the diagram it can

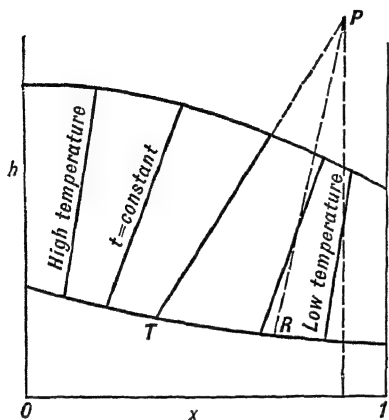


FIG. 176. The Polar Diagram
Showing temperatures of vapor and liquid in
rectifying column.

PT it coincides with a line of constant temperature. This is the condition of equilibrium of liquid and vapor, and the line PR can proceed no further.

The Plate Type of Rectifying Column

In practice a large surface of contact between liquid and vapor is obtained by bubbling the vapor through the liquid at intervals between the bottom and the top of the rectifier (Fig. 177). The liquid flows across trays while the vapor from below bubbles through it. The overflow of liquid from each tray is led down to the tray next below. Analyses of the processes in a column of this type may be found in the literature of chemical engineering.*

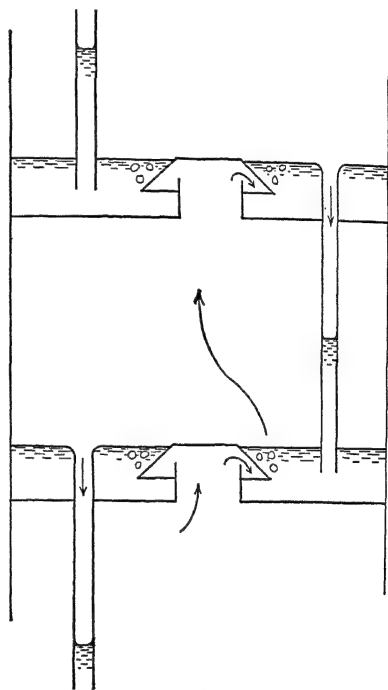


FIG. 177. Plate-Type Rectifying
Column

* See *Principles of Chemical Engineering*, Walker, Lewis, McAdams, and Gilliland, McGraw-Hill, 1937, Chapter XVI; and McCabe and Thiele, *Industrial and Engineering Chemistry*, Vol. 17 (1925), p. 600.

Equilibrium of Liquid and Vapor Phases at Different Pressures

It was pointed out above that Fig. 171 shows the relation between liquid and vapor phases for one particular pressure and that for a higher pressure the curves would be displaced upward. The pressure corresponding to Fig. 171 must be less than the critical pressure of either pure component, because a temperature of equilibrium of liquid and vapor is shown for each pure component.

To illustrate the effect of temperature and pressure on the relation between the liquid and vapor phases the phase boundaries for a binary system are shown on the pressure-temperature chart of Fig. 178.* The

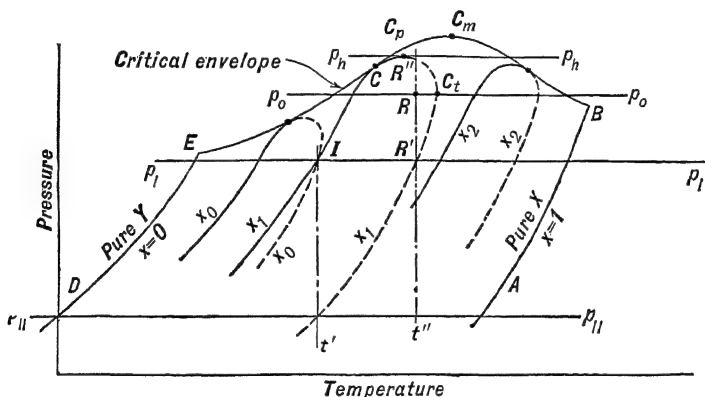


Fig. 178. Temperature Boundaries between Liquid and Vapor Phases of a Binary Mixture — Pressure-Temperature Diagram

line AB is the saturation line for pure component X , and the line DE is that for pure component Y . On either of these lines a point represents saturated liquid, saturated vapor, or any combination of the two. The extremities B and E of these lines represent the critical states of the pure components.

A mixture consisting of x_1 units (either mass units or moles) of substance X per unit of mixture will begin to boil at a given pressure p_l when its temperature reaches t' . The point p_l, t' is sometimes called a *bubble point* of the mixture of composition x_1 . Unlike a pure substance, a mixture cannot change from the liquid phase to the vapor phase without change in either pressure or temperature. In fact, if the mixture is heated at constant pressure sufficiently to vaporize it completely, the last of the liquid will vanish at a temperature t'' which is materially in excess of t' . Any further heating will superheat the

* For the phase relations of a ternary system see MacDougall, *Thermodynamics of Chemistry*, Wiley, 1926, pp. 239–244.

vapor. If the reverse process is considered it will readily be seen why the state p_l, t'' is sometimes referred to as a *dew point*. The curve in Fig. 178 labeled x_1 is the locus of all the bubble points and dew points of a mixture of composition x_1 .

A similar curve labeled x_0 and displaced to the left from the curve labeled x_1 is the locus of the bubble points and dew points for a mixture in which the proportion x_0 of substance X is less than x_1 . The curves of x_0 and x_1 cross at some point I . Therefore, at the pressure and temperature corresponding to point I two kinds of mixture can coexist — one of composition x_0 and one of composition x_1 . Of these two the

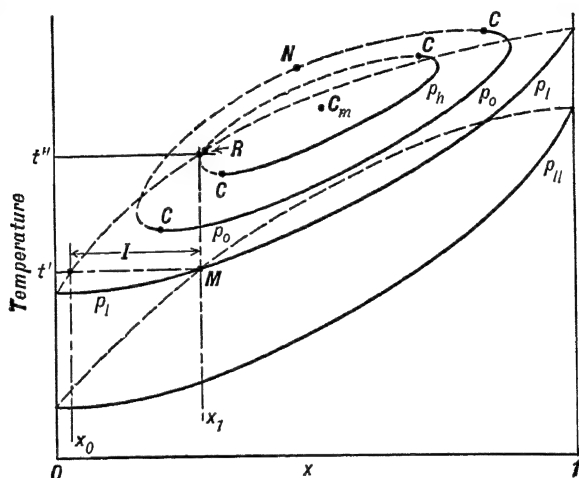


FIG. 179. Boundaries between Liquid and Vapor Phases of a Binary Mixture
Temperature-composition diagram.

mixture of composition x_0 is at a dew point and that of composition x_1 is at a bubble point: thus, the former is a vapor and the latter a liquid. By choosing compositions of the vapor intermediate between x_0 and x_1 the point of intersection I may be made to move upward along the curve x_1 . When it coincides with the point C the liquid and vapor are identical in composition and in phase, that is, they are indistinguishable. This is the true critical point of the mixture. Unlike a pure substance a mixture in the vapor phase may be caused to condense at some pressures at temperatures in excess of the critical temperature. The highest temperature at which liquid can be formed from a mixture of composition x_1 is that corresponding to the point C . A mixture can be caused to condense isothermally at some temperatures at pressures in excess of the critical pressure. The highest pressure at

which liquid can be formed from a mixture of composition x_1 is that corresponding to point C_p .

The relations between the phases which are shown on the p - t diagram of Fig. 178 may be transferred to the t - x diagram of Fig. 179. There the curves labeled p_h , p_0 , p_l , and p_{ll} show the compositions of states of saturated vapor and saturated liquid corresponding respectively to the pressures labeled p_h , p_0 , p_l , p_{ll} in Fig. 179. In both Figs. 178 and 179 saturated liquid states lie on the solid lines and saturated vapor states on the broken lines. In Fig. 179 liquid and vapor states that can coexist lie horizontally opposite each other on a line of constant pressure. Thus at pressure p_l and temperature t' the vapor and liquid that can coexist have respectively the compositions x_0 and x_1 . The points marked C in Fig. 179 are critical states, and the locus of these points corresponds to the "critical envelope" of Fig. 178.

A point such as M in Fig. 179 may represent a saturated liquid at pressure p_l or a saturated vapor at a lower pressure p_{ll} . Thus a saturated vapor may be condensed isothermally by the application of pressure. If the pressure is raised to the value of p_0 there are saturated vapor states such as N (Fig. 179) which cannot be condensed by isothermal compression. For an increase of pressure to p_h causes the closed saturation curve of Fig. 179 to contract so that the temperature at N is in excess of that of saturated vapor of the same composition, and the state N is therefore a superheated one.

Retrograde Condensation

For a given composition x_1 at any temperature between the critical temperature (corresponding to C , Fig. 178) and the maximum temperature of condensation (corresponding to C_t) a phenomenon can be observed that is known as *retrograde condensation*. Let us consider the point R in Fig. 179. The isothermal corresponding to the temperature at R is labeled $R'R''$ in Fig. 178 and lies between the critical temperature and the maximum temperature of condensation for a mixture of composition x_1 . It can be seen from Figs. 178 and 179 that the point R corresponds to two saturated vapor states, one, R' , at pressure p_l , and the other, R'' , at pressure p_h . At a pressure p_0 intermediate between p_l and p_h the point R lies within the line of saturation states (Fig. 179) and therefore represents a two-phase state. It follows that if a saturated vapor in state R' (Fig. 178) is compressed isothermally some condensation will occur; but if it is compressed still further the liquid will evaporate. The formation of the liquid under these circumstances is called retrograde condensation. A similar effect may be

observed by cooling or heating a mixture of composition x_1 at a pressure intermediate between the pressures of states C and C_p .

Retrograde Vaporization

For values of x near unity the curve of saturation states may take a form like that labeled x_2 in Fig. 178. A line of constant pressure intermediate between the pressure of the critical point and the maximum pressure for this curve would intersect the liquid curve at two points.

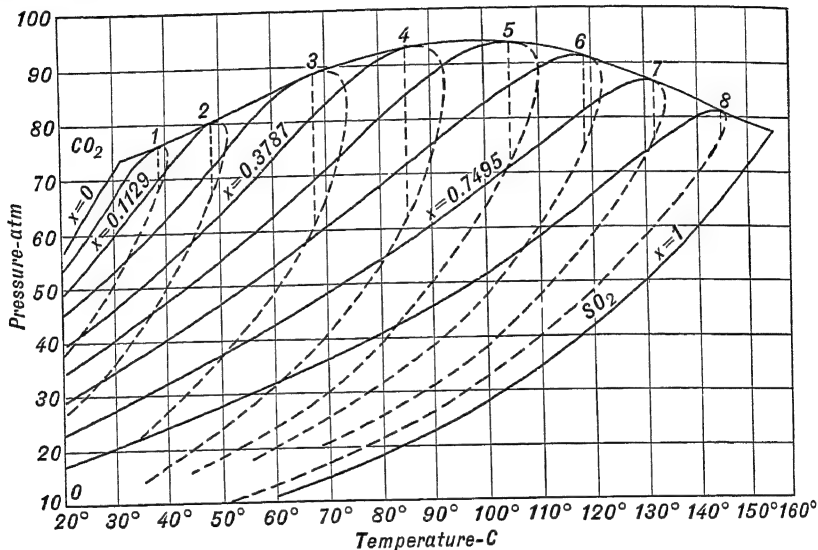


FIG. 180. Boundaries between Liquid and Vapor Phases for the System $\text{CO}_2\text{-SO}_2$
From Caubet, *Z. Phys. Chem.*, Vol. 40 (1902), p. 284.

Between these two points the line would represent two-phase states which could be reached by heating at constant pressure from one saturated liquid state or by cooling from the other. The formation of vapor under these circumstances is called *retrograde vaporization*.

The curves of Figs. 178 and 179 have exaggerated characteristics for purposes of illustration. Figure 180 shows an actual pressure-temperature diagram for the binary system $\text{SO}_2\text{-CO}_2$.

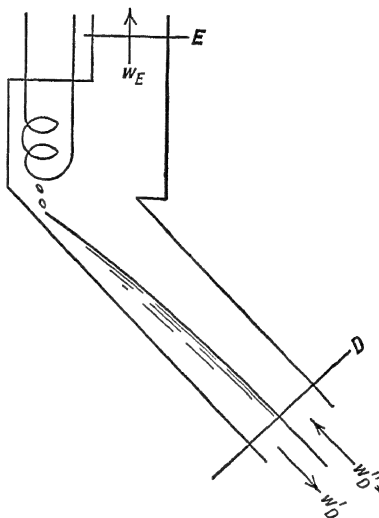
PROBLEMS

In the following problems data relative to mixtures of ammonia and water may be obtained from Jennings and Shannon, *Refrigeration Engineering*, Vol. 35 (1938), pp. 333-336.

1. (a) A mixture of vapor is introduced into the apparatus shown in the sketch at section D . The volatile component is removed at E as a pure vapor.

Find an expression in terms of concentrations of vapor and liquid at D for the mass that flows out at E per unit mass of vapor entering at D .

(b) Plot the flow out at E against the composition of a mixture of water and ammonia vapors that enter at D at a pressure of 100 lb/sq in. abs. Assume the liquid and vapor at D to be in equilibrium.



2. (a) Find an expression for the minimum rate of vaporization at G in the column of Fig. 172 per unit rate of flow at A . Assume complete rectification, and give the expression in terms of the latent heats L_A and L_0 , and properties at D and G .

(b) Give the expression for the minimum rate of heat transfer at H .

3. A mixture of ammonia and water in the liquid phase having 20 per cent ammonia by mass and at the bubble-point temperature is introduced into a column like that of Fig. 173 at 100 lb/sq in. abs.

Find for complete rectification of 1 lb of liquid and for equilibrium between vapor and liquid at section D :

- The reflux at section D .
- The flow of pure ammonia out at E .
- The flow of pure water out at G .
- The heat taken out at C .
- The heat put in at H .

4. Describe the polar diagram for the lower half of the column of Fig. 173.

If the column of Fig. 173 has liquid and vapor in equilibrium at section D , show the polar diagram with the two poles. Show the lines corresponding to section D . Sketch in the isotherms.

5. Plot a polar diagram for ammonia-water mixtures at a pressure of 100 lb/sq in. abs. Let the liquid at A be 15 per cent ammonia, the vapor at E 98 per cent ammonia, and the liquid at G 3 per cent ammonia. Assume equilibrium of liquid and vapor at D .

- Find from your chart the heat quantities at C and H .
- Show the isotherms and the lines corresponding to sections through the column.
- Plot a curve showing temperature of the vapor as ordinate and temperature of the liquid as abscissa for sections along the column.
- Plot a t - x diagram showing liquid and vapor. Connect with straight lines the liquid and vapor states corresponding to different sections along the length of the column.
- If pure liquid and vapor were discharged at E and G how would these data and diagrams be altered?

6. Sketch the pressure-composition diagram corresponding to Figs. 178 and 179, showing isotherms for temperatures less than the lowest critical temperature and intermediate between the critical temperatures of the pure constituents.

Construct also a diagram having composition of the vapor as ordinate and that of the liquid as abscissa.

SYMBOLS

h	enthalpy per unit mass
L	latent heat of vaporization
m	mass
p	pressure
q	heat transferred per unit of mass discharged
Q	rate of transfer of heat
t	temperature
w	rate of flow per unit rate of inlet flow
x_1	the proportion of substance 1 in a mixture ($= m_1/m$)

SUBSCRIPTS

E	vapor leaving top of column
G	liquid leaving bottom of column

SUPERSCRIPTS

'	liquid
"	vapor

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CHAPTER XXIII

THE CRITERIA OF EQUILIBRIUM

Equilibrium

A system is said to be in a state of *equilibrium* if no active unbalanced tendency toward a change of state exists. A system is not in a state of equilibrium if a change of state will occur spontaneously and without the aid of a disturbance, finite or infinitesimal. We shall call such a state a non-equilibrium state.

Thus, a system consisting of a marble and a bowl is in a state of equilibrium if the marble is at rest at the bottom of the bowl. If, on the other hand, the marble is rolling about in the bowl the system is in a non-equilibrium state, because it will gradually change toward the state of equilibrium even if left undisturbed.

Stable and Unstable Equilibrium

If the bowl is inverted and the marble is balanced on top of it, the system is in a state of equilibrium. But this type of equilibrium is distinctly different from that corresponding to the marble in the bottom of the bowl. In the latter case a small disturbance will cause only a temporary change in the state of the system; in the former, even an infinitesimal disturbance will cause a sweeping change.

A state of equilibrium that will persist despite disturbances is a stable state. A state of equilibrium that will not survive infinitesimal disturbances is an unstable state. Other kinds of equilibrium will be defined subsequently, but of all these the stable kind is by far the most important. Let us try to discover a criterion, the *criterion of stability*, by means of which a state of stable equilibrium may be identified.

First we shall consider a simple mechanical system made up of incompressible parts, free from the influence of electricity and magnetism, and not subject to chemical change. If such a system is not in a stable state it may change its state spontaneously unaided except by an infinitesimal disturbance. On the other hand, if it is in a stable state it can change to other states only if it receives work from some external source.

Possible Variations

A change from one state of a system to another state which is possible in view of the description of the system is called a *possible variation*.

Thus, for the bowl and marble, possible variations include any change in the position or speed of the marble within the bowl; but they do not include a change in the position of the marble that could be realized only if the marble were to pass through the wall of the bowl, for it was implied above that the bowl is made of a firm, unyielding material. If it were made of beeswax the marble would pass spontaneously, though slowly, through the bottom of the bowl, and no stable state would be reached until it had come to rest on an unyielding surface. Therefore, *a possible variation is any change of state that can be accomplished without destroying the system.*

Stability of a Mechanical System

The criterion of stability for the mechanical system may now be stated in the following form: a mechanical system is in a state of stable equilibrium if for all possible variations work must flow to it. Thus, for the bowl and marble, if there is a possible variation which results in a lesser speed or a lower position of the marble then work can be caused to flow from the system by using a suitable mechanism for slowing down the marble or for lowering it, as the case may be. Therefore the system is not in stable equilibrium. If, on the other hand, the marble is at rest at the bottom of the bowl, for all possible variations in the position or speed of the marble work must flow to the system.

Since for each possible variation from the stable state no heat need flow into or out of a mechanical system, the flow of work measures the change in the internal energy of the system. Therefore we may express this criterion of stability as follows: a mechanical system is in a state of stable equilibrium if for all possible variations

$$\Delta E > 0, \quad [236]$$

where ΔE denotes the *variation* in energy in the algebraic sense, that is, the difference between the energy of the system after the variation and that before. The quantity ΔE includes small quantities of all orders as well as finite quantities. Thus, if the marble is at the bottom of the bowl an infinitesimal lateral displacement of the marble would require an amount of work of the second order of small quantities. If then we let δE denote the variation in energy to the same order as the displacement, we get for some infinitesimal displacements

$$\delta E = 0,$$

though for the same displacements

$$\Delta E > 0.$$

On the other hand, if the marble were wedged into a cone with apex downward, then for stable equilibrium

$$\delta E > 0$$

for all possible variations. Consequently, for an equilibrium state

$$\delta E \geq 0$$

for all possible variations. The *inequality* is a sufficient condition for stable equilibrium though not a necessary one. The *equality* is neither necessary nor sufficient, but it is frequently employed as a criterion when changes in state with small variations are known to be continuous.

The Criterion of Stable Equilibrium

The criterion of stability for a mechanical system is a special case of the more general criterion of equilibrium provided by thermodynamics for any system. The general criterion is a direct consequence of Corollary 6 of the Second Law; namely, *the entropy of an isolated system increases or in the limit remains constant*. If there are possible variations in the state of an isolated system for which the entropy increases, those variations can occur. If, on the other hand, the state of the system is such that for all possible variations the entropy decreases, then none of these variations can occur and the system is in a state of stable equilibrium. Thus the general criterion of stable equilibrium is as follows: *For the stability of any isolated system it is necessary and sufficient that, in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall be negative*. More briefly:

$$\Delta S) < 0, \quad [237]$$

where $\Delta S)_E$ denotes the variation in entropy at constant internal energy to all orders of small quantities. Constant internal energy is required, of course, by the isolation of the system of Corollary 6.

Applications of the Criterion

Some simple applications of the criterion [237] to thermodynamic systems will serve to show the analytical technique involved in the test for equilibrium:

First, let us consider a system comprising two blocks of copper at different temperatures and in contact. A possible variation at constant energy consists of a small decrease in the energy of the hotter block and an equal increase in the energy of the colder one. Since the energy of a

block of copper can be changed reversibly by a flow of heat equal in magnitude to the change in energy (if changes in volume can be ignored), the variation in the entropy of the hot block is given by

$$\frac{\delta E}{T_1},$$

and that of the cold block by

$$\frac{\delta E}{T_2},$$

where δE denotes the variation in energy of the cold block, and T_1 and T_2 denote respectively the mean temperatures of the hot and cold blocks during the variation. The variation in the entropy of the whole system is then given by

$$\Delta S \Big|_E = \delta E \left(\frac{1}{T_2} - \frac{1}{T_1} \right),$$

and, therefore,

$$\Delta S \Big|_E > 0$$

and the system is not in stable equilibrium.

On the other hand, if the two blocks are originally at the same temperature and the only possible variation is a variation in the energies of the individual blocks, then we may show by the same test that stable equilibrium subsists. The mean temperature of the block whose energy decreases during the variation is less than T , the temperature of the system, and may be written $(T - dT)$, whereas that of the other is greater than the temperature of the system and may be written $(T + dT)$. The variation in the entropy of the whole system is then

$$\Delta S \Big|_E = \delta E \left(\frac{1}{T + dT} - \frac{1}{T - dT} \right) < 0.$$

Therefore, the variation cannot occur and the system is in stable equilibrium.

No system with parts at different temperatures is in stable equilibrium because there is always a possible variation at constant energy for which the entropy of the system increases. A system which is uniform in temperature is in stable equilibrium provided that variations in energy of its parts constitute all possible variations.

Next let us consider a system comprising a fluid moving at various velocities within a closed chamber. The energy E of such a system is made up of two parts, namely, internal energy, irrespective of motion

and position, and kinetic energy. In terms of the usual symbols

$$E = \int \frac{V^2}{2g} dm + \int u dm.$$

A possible variation is a reduction in velocity, which at constant internal energy must result in an increase in the second term of the expression for E and therefore an increase in u . But from the First and Second

$$du = T ds - p dv.$$

Since the variation requires no change in volume we find that

$$du = T ds,$$

and the entropy increases with the quantity u . Therefore, we have found a possible variation for which

$$\Delta S \Big|_E > 0,$$

and the system is not in stable equilibrium. It follows that no system with parts at different velocities is in stable equilibrium because there is always a possible variation toward uniformity of velocity for which the entropy of the system increases.

Finally, let us consider a system consisting of a fluid which is in a container and separated by a diaphragm from an exhausted space. If the diaphragm is punctured a possible variation consists of a transfer of some of the fluid into the exhausted space. The direction of the change in entropy for a variation of this sort at constant energy can be determined by executing the same change of state reversibly. For example, let a piston which is initially flat against the punctured diaphragm (Fig. 181) move out slowly until the amount of fluid corresponding to the variation has passed through the orifice. Now close the orifice and let the piston move out slowly until the entire volume of the initially evacuated space is filled by the fluid. The volume occupied by the fluid which

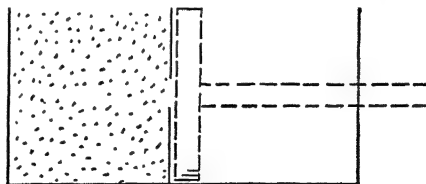


Fig. 181

passed through the orifice is now the same as after the proposed variation; but because of the work done by it on the piston the energy of the system is less. Now it is always possible to increase the energy of a system at constant volume by heating. Therefore the

system can be brought to a state having an energy identical with its initial energy. Since the entire process described is reversible, the change in entropy can be found in terms of the heat:

$$\Delta S = \int \frac{dQ}{T} > 0.$$

Furthermore, this change in entropy occurs between two states for which the energy of the system is the same. Therefore, there is a possible variation for which

$$\Delta S \Big|_E > 0,$$

and the system is not in stable equilibrium.

It can be shown as readily that, if the fluid fills the chambers on either side of the diaphragm at uniform pressure, a variation consisting of a transfer of mass at constant energy would result in a decrease in entropy. The system would therefore be stable as regards this sort of variation.

An Alternative Criterion

The first part of the reversible operation described above indicates that there is a possible reversible adiabatic variation for which work flows from the system. That is, the criterion of mechanical equilibrium can be applied equally well to this case if that criterion is expressed in the following form: *A system is in a state of stable equilibrium if for all possible variations*

$$\Delta E \Big|_S > 0. \quad [238]$$

The two criteria [237] and [238] are entirely equivalent in all cases. The proof of this statement follows:

Assume that a system can be found in a state for all possible variations of which

$$\Delta E \Big|_S > 0,$$

but for at least one possible variation

$$\Delta S \Big|_E > 0.$$

That is, there is at least one possible variation for which $\Delta S > 0$ and $\Delta E = 0$. But it is always possible to increase E and S by a flow of heat to the system or to decrease both by a flow of heat from the system.

Therefore, by combining the variation for which $\Delta S > 0$ and $\Delta E = 0$ with one for which $\Delta S < 0$ and $\Delta E < 0$ a possible variation can be found for which $\Delta S = 0$ and $\Delta E < 0$. But this is contrary to our first assumption. Therefore if condition $\Delta S \Big|_E < 0$ is not satisfied then condition $\Delta E \Big|_S > 0$ is not satisfied. By similar reasoning it can be shown that if condition $\Delta E \Big|_S > 0$ is not satisfied then condition $\Delta S \Big|_E < 0$ is not satisfied. It follows that if one of the two conditions is satisfied the other must also be satisfied,* and the two conditions are entirely equivalent.

Other Criteria of Stability

By means of one or the other of the criteria [237] and [238] we have shown that it is *necessary* for the stability of a system that it should be uniform in temperature, and (in the absence of gravity, electricity, capillarity, and magnetism) uniform in pressure.

For any system that is uniform in temperature it is *necessary and sufficient* for stability that for all possible variations without change in temperature

$$\Delta \Psi \Big|_T > 0, \quad [239]$$

where $\Delta \Psi$ denotes the variation in the quantity

$$\Psi = E - TS.$$

For any system that is uniform in temperature and pressure it is *necessary and sufficient* for stability that for all possible variations without change in temperature or pressure

$$\Delta Z \Big|_{T,p} > 0, \quad [240]$$

where ΔZ denotes the variation in the quantity

$$Z = E + pV - TS,$$

V denoting the volume of the system.

* If one is satisfied and the other is not then we have one of the propositions which can be proved impossible by the reasoning given above. There is only one alternative; namely, if one is satisfied the other is also satisfied.

The criteria $\Delta S \Big|_E < 0$, $\Delta E \Big|_S > 0$, and $\Delta \Psi \Big|_T > 0$ are entirely equivalent to each other. If a system is in a stable state according to one it is in a stable state according to the others. They differ only in the nature of the test for stability. In each test, however, it is assumed that the system is bounded by a rigid container which sets an upper limit to the volume of the system; otherwise states could always be found with less energy at the same entropy.

In the test implied by the criterion $\Delta Z \Big|_{T, p} > 0$ the boundary is not fixed but only the pressure at the boundary. This test is somewhat less general in its application because it can be applied only where stability involves uniformity of pressure. It cannot be applied, for instance, to a column of liquid in a gravitational field. But where stability demands uniformity of pressure [240] is entirely equivalent to the other three.

It should be noted that the criterion

$$\Delta E \Big|_S > 0 \quad [238]$$

is equivalent to the statement that in any reversible adiabatic variation work must flow to the system. The criterion

$$\Delta \Psi \Big|_T > 0 \quad [239]$$

is equivalent to the same statement as regards isothermal variations. The criterion

$$\Delta Z \Big|_{p, T} > 0 \quad [240]$$

is equivalent to the statement that in any reversible isothermal and isopiestic variation work in excess of the work done by the envelope which maintains the pressure p must flow to the system.

If a system is exposed to an indefinitely large environment or medium which has a uniform pressure p_0 and a uniform temperature T_0 , and is separated from it by an envelope which in itself offers no resistance to expansion or contraction, then the maximum net work that could be done by the system and medium during any change of state is the decrease in the availability function.* The criterion of stability may therefore be stated in the following form: In any possible variation which does not alter the pressure and temperature of the medium, work

* See Chapter XVII.

must flow to the system and medium. This is equivalent to a new criterion

$$\Delta\beta\bigg)_{p_0, T_0} > 0, \quad [241]$$

where

$$\beta = E + p_0V - T_0S,$$

and E , V , and S are respectively the energy, volume, and entropy of the system.

Kinds of Equilibrium

A system is in a state of *stable equilibrium* if for all possible variations

$$\Delta S\bigg)_E < 0; \text{ that is, } \Delta E\bigg)_S > 0.$$

A marble at rest in the bottom of a bowl is an example of a system in stable equilibrium (Fig. 182).

A system is in a state of *neutral equilibrium* if there are some possible variations in the state of the system for which

$$\Delta S\bigg)_E = 0, \text{ that is, } \Delta E\bigg)_S = 0;$$

while for possible variations in general

$$\Delta S\bigg)_E \leq 0, \text{ that is, } \Delta E\bigg)_S \geq 0.$$

A marble at rest in the bottom of a horizontal trough is an example of neutral equilibrium (Fig. 183).



FIG. 183

A system is in a state of *unstable equilibrium* if there is at least one infinitesimal variation for which

$$\Delta S\bigg)_E > 0, \text{ that is, } \Delta E\bigg)_S < 0,$$

while for infinitesimal variations in general

$$\delta S\bigg)_E \leq 0, \text{ that is, } \delta E\bigg)_S \geq 0.$$

It should be recalled that δ denotes a variation of the same order as the

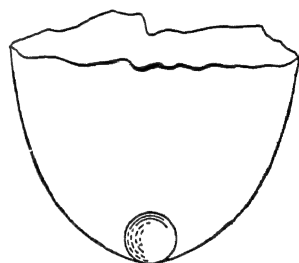


FIG. 182

variation in the state of the system; higher orders are not included. On the other hand, Δ denotes a variation of any order, higher orders included. A marble at rest at the highest point in the trough of a saddle (a trough bent so that its open side is convex in the plane of bending) is an example of unstable equilibrium (Fig. 184). For all possible infinitesimal variations in the position of the marble the variation in E is zero to the same order as the variation, but for longitudinal variations in position the variation in E is negative if small quantities of higher orders are considered.

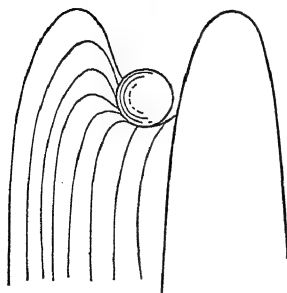


FIG. 184

A system is in a state of *metastable equilibrium* if for all infinitesimal possible variations

$$\Delta S \Big|_E < 0, \quad \text{that is,} \quad \Delta E \Big|_S > 0,$$

while for some finite possible variations

$$\Delta S \Big|_E > 0, \quad \text{that is,} \quad \Delta E \Big|_S < 0.$$

A marble at rest at the bottom of the higher of two depressions in a continuous surface is an example of metastable equilibrium (Fig. 185). No infinitesimal disturbance will cause the marble to seek a new position, but a disturbance large enough to take it to the top of the intervening hump may cause it to find a new and more stable position in the lower depression.



FIG. 185

Passive Resistance

If an equilibrium state is defined as a state which does not permanently change as a result of either infinitesimal or of finite disturbances then

we know from experience that the condition $\Delta S \Big|_E < 0$ [or $\Delta E \Big|_S > 0$]

for all possible variations is not necessary to equilibrium. For example, a block may be at rest on an inclined surface. A possible variation of the state of the system is a change of the position of the block downward

along the surface. For this variation

$$\Delta E \Big|_s < 0,$$

and the criterion of equilibrium is not satisfied. Nevertheless, as a result of static friction no change in the position of the block occurs for infinitesimal disturbances or for some finite disturbances. A force or a resistance, such as the friction in this instance, which prevents a change in the state of a system toward stable equilibrium is known as a *passive force* or a *passive resistance*.

A passive resistance can usually be recognized because it prevents a certain kind of motion or change despite finite changes in the initial state of the system or in external agents which are in temperature equilibrium with it or apply forces to it. Usually the changes which can occur without causing the system to execute the motion or change in question are limited in magnitude though they may be finite. For example: hydrogen and oxygen can coexist as a mixture of gases at room temperature and pressure, even though in the presence of a catalyst they unite to form water, a more stable state. No ordinary finite disturbance like an alteration in temperature will cause the system to change from a mixture of elements to a single compound, provided that the alteration in temperature is not so great as to cause "ignition." The equilibrium is, consequently, the result of passive resistance.

In true stable equilibrium, on the other hand, an external influence or a change in the initial state, infinitesimal in amount, is sufficient to produce change in one direction, while a reversal of the influence or of the direction of the change in the initial state will produce change in the opposite direction. In a lead storage cell, for example, the tendency toward chemical reaction may be completely neutralized by applying an electromotive force across the terminals of the cell. If the electromotive force is reduced, lead will be consumed at the lead plate; if it is increased, lead will be deposited. When reaction occurs in neither direction there is a balance of active tendencies and the system is in a state of true equilibrium.

The criterion of stability, $\Delta S \Big|_E < 0$, that is $\Delta E \Big|_S > 0$, for all possible

variations, is *sufficient* to insure equilibrium. It is not, however, *necessary* to equilibrium where neutral equilibrium or passive resistance is involved. Neutral equilibrium and unstable equilibrium are seldom encountered in analysis and less often in practice. They are of little consequence because they never persist. On the other hand, equilibrium due to passive resistance occurs commonly.

PROBLEMS

1. Show that if a fluid fills the chambers on either side of a punctured diaphragm, with uniform temperature and pressure throughout, the system is in a stable state as regards variations in temperature or mass on either side of the diaphragm.

2. Show that if the condition $\Delta E)_S > 0$ is not satisfied for all possible variations then the condition $\Delta S)_E < 0$ is not satisfied for all possible variations.

3. Show by means of the criterion $\Delta S)_E < 0$ for all possible variations, that (a)

a marble at rest in the bottom of a bowl is in a state of stable equilibrium, (b) that a marble at rest anywhere else in the bowl is not in a state of stable equilibrium, and (c) that if a marble is in motion in the bowl it is not in a state of stable equilibrium.

4. Show by each of the criteria [237], [238], [239], and [240] in turn that a fluid that is exposed to an environment of constant and uniform pressure and temperature is not in a stable state if there is relative motion between the parts of the fluid.

5. Show by means of the criterion $\Delta E)_S > 0$ that two copper blocks having different temperatures do not constitute a system in a state of stable equilibrium.

6. By means of the criterion $\Delta \Psi)_T > 0$ show that a system consisting of two masses of gas at the same temperature and separated by a punctured diaphragm are not in stable equilibrium unless the pressure is the same on both sides of the diaphragm.

7. For a substance in equilibrium with an environment of constant and uniform pressure and temperature, how does the most stable state compare with the "dead state" referred to in Chapter XVII?

SYMBOLS

E	internal energy of a system
m	mass
p	pressure
Q	heat to system
s	entropy per unit mass
S	entropy of system
T	absolute temperature
u	internal energy of a unit system in the absence of motion, gravity, etc.
v	specific volume
V	volume

GREEK LETTERS

β	$(E + p_0 V - T_0 S)$
δ	variation of same order as variation in state of system

Δ	variation of any order
Ψ	$(E - TS)$
Z	$(E + pV - TS)$

SUBSCRIPTS

E	constant internal energy
o	environment
p	constant pressure
S	constant entropy
T	constant temperature

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CHAPTER XXIV

EQUILIBRIUM OF A PURE SUBSTANCE

A pure substance may assume states of all degrees of stability and instability. Only those that are states of equilibrium will persist, and of these only states of stable equilibrium will persist despite disturbances. In this chapter we shall deduce means by which we may recognize a state of equilibrium and classify it as regards stability. Moreover, we shall show in what ways the relations between properties of the substance are restricted by the requirements of equilibrium.

The Conditions for Equilibrium

Let us state the requirements for stable equilibrium in terms of the ratios of variations in properties. Using Δ to denote small quantities of all orders, we have

$$\left[\frac{\Delta s}{\Delta T} \right]_T > 0 \quad [242a]$$

and

$$\left[\frac{\Delta p}{\Delta v} \right]_s < 0. \quad [242b]$$

The first of these states in effect that when heat is added reversibly at constant pressure the temperature must increase; the second that when the pressure is increased reversibly and adiabatically the volume must decrease. It should be noted that the partial derivative $(\partial s / \partial T)_p$ is the limit of $[\Delta s / \Delta T]_p$ as ΔT approaches zero. The condition [242a] does not, therefore, exclude all instances for which $(\partial s / \partial T)_p = 0$, but only those for which $(\partial s / \partial T)_p = 0$ over more than an infinitesimal range of states and those for which s is at a maximum or a minimum. The condition is not contravened if the partial derivative is zero at a point of inflection in a curve of s against T having in general $(\partial s / \partial T)_p > 0$. Similar comments might be made concerning condition [242b].

The Necessity of the Conditions

We shall prove that condition [242a] is *necessary* to stable equilibrium of a pure substance by considering a possible variation in the state of a system composed of a pure substance which is enclosed in a rigid con-

tainer. The possible variation will consist of a variation in temperature δT of a very small part of the system while the energy of the system as a whole remains unaltered. This might be accomplished reversibly by adding to the small part an amount of heat δq and taking from the large remaining part the same amount of heat.

Now, if we let δs denote the variation in the entropy of the small part, the heat involved in the reversible process is

$$(T + \frac{1}{2} \delta T) \delta s$$

to a satisfactory degree of approximation. The variation in the entropy of the large part, δS , is, therefore,

$$-(T + \frac{1}{2} \delta T) \frac{\delta s}{T},$$

because its temperature is affected only to smaller orders than δT . The variation in the entropy of the entire system is now given by

$$\delta s + \delta S = -\frac{1}{2} \frac{\delta T}{T} \delta s \quad [243]$$

Since the variation δT in a very small part cannot affect the pressure of the whole to the same order of magnitude as that of δT , we may consider the variation in the small part to have occurred at constant pressure. Let us assume that condition [242a] is not satisfied: that is,

$$\left[\frac{\Delta s}{\Delta T} \right]_p \leq 0.$$

Then it follows that δs and δT have opposite signs or else δs is zero for all values of δT . Combining these conditions with [243] we get

$$\delta s + \delta S \geq 0.$$

But for stable equilibrium the entropy of the system must decrease for all possible variations at constant energy. Therefore, the system is not in stable equilibrium.

It should be noted that the condition [242a] is equivalent to the requirement that the specific heat at constant pressure shall not be less than zero, because

$$c_p = T \left(\frac{\partial s}{\partial T} \right)_p \quad [196]$$

A substance with negative specific heat would sweep to a non-homogeneous condition; because any slight accidental change in the temperature of a part would result in a flow of heat from the warmer part to the cooler

part, the flow of heat would increase the difference in temperature which would in turn increase the flow of heat.

We shall prove that condition [242b] is *necessary* to stable equilibrium of a pure substance by considering another possible variation in the state of a pure substance which is enclosed in a rigid container or envelope. It will consist of an isentropic variation in volume δv of a very small part of the system while the entropy of the system as a whole remains unaltered. This could be accomplished by enclosing the small part in a rigid non-conducting cylinder having a piston, with a piston rod extending through the envelope of the system (Fig. 186). (The mechanism

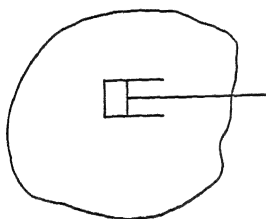


Fig. 186

may be assumed to occupy a smaller order of space than the part of the system which it encloses.) The proposed variation would be accomplished by a slow motion of the piston. During this process the pressure exerted on the piston by the part it confines varies by an amount δp ; but the pressure exerted on the outside of the piston by the larger part changes by an amount which is negligible

as compared with δp . To attain slow motion it is necessary to apply an external force to the piston rod. As a result of the process the variation in the energy of the system, which is equal to the work received by it, is

$$\Delta E = -\frac{1}{2} \delta p \delta v \quad [244]$$

to a satisfactory degree of approximation.

Let us assume that condition [242b] is not satisfied: that is,

$$\left[\frac{\Delta p}{\Delta v} \right]_s \geq 0.$$

Then it follows that δp and δv have identical signs (one is positive if the other is positive) or else δp is zero for all values of δv . Combining these alternatives with [244] we get

$$\Delta E \leq 0$$

for a possible variation for which the entropy of the system does not change. The system is, therefore, not in a state of stable equilibrium.

A substance for which

$$\left[\frac{\Delta p}{\Delta v} \right]_s > 0$$

could not be in equilibrium with a piston or an environment which exerts a constant pressure. Any slight accidental inward motion of the piston

would result in a decrease in the pressure exerted on the piston. The piston would, therefore, move inward with increasing acceleration, because the further it moves the less the force opposing its motion.*

The Sufficiency of the Conditions

It has been shown that conditions [242a] and [242b] are *necessary* for the stability of a system consisting of a pure substance in the absence of gravity, capillarity, electricity, and magnetism. It is also necessary that the system should be in equilibrium with its immediate environment as regards pressure and temperature and that there should be no relative motion. But all these conditions taken together are *sufficient* conditions for stability. For, under these conditions, the only possible variations are those associated with a transfer of heat or a change in volume. To avoid instability with respect to either of these types of variation it is necessary and sufficient that [242a] and [242b] should be satisfied.

States for Which $(\partial p/\partial s)_v$ Is Greater than Zero

The restrictions imposed by the requirements of equilibrium on the relation between properties we shall show by the method of Gibbs in which is determined the arrangement about a point of lines along which different properties are constant. We shall also follow Gibbs in first arbitrarily classifying states of substances according to whether the derivative $(\partial p/\partial s)_v$ is positive, negative, or zero.

Consider a state of a pure substance for which

$$\left(\frac{\partial p}{\partial s}\right)_v > 0.$$

* There are four conditions for neutral equilibrium, which can be stated as follows:

1. $[\Delta T/\Delta s]_p = 0$. The specific heat at constant pressure is infinite over a finite range of states. An example is a system consisting of ice and liquid water in an equilibrium state. If confined at constant volume in an insulated container any one piece of ice may grow at the expense of any other.
2. $[\Delta s/\Delta T]_p = 0$. The specific heat at constant pressure is zero over a finite range of states. Such a system while confined at constant pressure could drift to a higher or lower temperature reversibly and adiabatically.
3. $[\Delta p/\Delta v]_s = 0$. The quantity $(\partial p/\partial v)_s$ is zero over a finite range of states. Such a system while confined at constant pressure could drift to a larger or smaller volume reversibly and adiabatically. An example is a mixture of three phases at the triple point.
4. $[\Delta v/\Delta p]_s = 0$. The quantity $(\partial v/\partial p)_s$ is zero over a finite range of states. This is the truly incompressible fluid. The pressure it exerts on the walls of a rigid container could drift up or down reversibly and adiabatically.

From these considerations it will be seen that for stable equilibrium $[\Delta s/\Delta T]_p$ is greater than zero but not infinite, and $[\Delta p/\Delta v]_s$ is less than zero but not infinite.

It follows then from Maxwell relation [190c] that

$$\left(\frac{\partial T}{\partial v}\right)_s < 0.*$$

Since $(\partial p/\partial s)_v$ does not vanish there is a definite isopiestic passing through the point representing this state on any diagram of properties, and on one side of this isopiestic the pressures are greater and on the other

side less than on the line itself. As $(\partial T/\partial v)_s$ does not vanish the case is the same with the isotherm.

If we choose to represent these lines on a diagram with pressure as ordinate and temperature as abscissa then we may represent the point as the intersection of an isopiestic pp' and an isotherm TT' which are mutually perpendicular (Fig. 187). Following the usual convention we indicate by a plus sign above the isopiestic that pressures are higher on that side of the line, and by a minus sign below it that pressures are lower

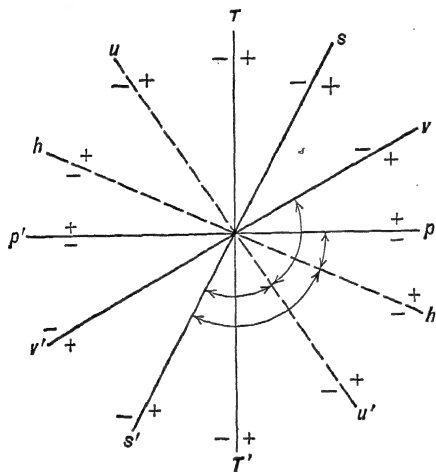


FIG. 187. Arrangement of Lines about a Point for $(\partial p/\partial s)_v > 0$

there. The directions of higher and lower temperature are similarly indicated by plus and minus signs on the isotherm.

The conditions of stability [242a] and [242b] are satisfied if $(\partial s/\partial T)_p$ is greater than zero or is equal to zero at a point of inflection, and if $(\partial p/\partial v)_s$ is less than zero or is equal to zero at a point of inflection. Omitting for the present the exceptional cases for which these derivatives vanish, we may write the requirements for the state in question as follows:

By assumption

$$\left(\frac{\partial p}{\partial s}\right)_v > 0 \quad [m]$$

and

$$\left(\frac{\partial T}{\partial v}\right)_s < 0; \quad [n]$$

* This is the common case. Only occasionally does one encounter the opposite case, liquid water below 4 C being one of the few examples.

for stability

$$\left(\frac{\partial s}{\partial T}\right)_p > 0 \quad [p]$$

and

$$\left(\frac{\partial p}{\partial v}\right)_s < 0. \quad [q]$$

Combining $[n]$ and $[q]$, we get

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial v}{\partial p}\right)_s > 0.$$

Therefore the isentropic ss' passes through the point from the minus-minus quadrant to the plus-plus quadrant (southwest to northeast). According to $[p]$ the under side of line ss' is the plus side.

The isometric vv' must lie between the plus side of ss' and the plus side of pp' according to $[m]$. The under side of vv' is the plus side according to $[n]$.

Something can be learned from these same requirements about the positions of the lines of constant internal energy and constant enthalpy. Recalling that

$$= \frac{du}{T} + \frac{p}{T} dv,$$

we get

$$\left(\frac{\partial s}{\partial v}\right)_u = \frac{p}{T} > 0$$

for any gas and for a liquid that is not supporting tension. Therefore, the line of constant internal energy uu' can lie anywhere except in two sectors, namely, the one bounded by the minus side of vv' and the plus side of ss' and the opposite one. The fact that the internal energy must increase with the entropy at constant volume determines the plus side of uu' .

From the equation

$$\frac{dh}{T} = \frac{v}{T} dp$$

it follows that

$$\left(\frac{\partial s}{\partial p}\right)_h = -\frac{v}{T} < 0.$$

Therefore, the line of constant enthalpy hh' can lie anywhere except in

two sectors, namely, the one bounded by the plus sides of the isentropic and the isopiestic and the opposite one. The fact that the enthalpy must increase with the entropy at constant pressure determines the plus side of hh' .

Though Fig. 187 yields much information concerning the signs of the partial derivatives, it leaves some questions unanswered. It appears, for example, that neither the assumed condition nor the conditions of stability specify the sign of either the Joule coefficient $(\partial T/\partial p)_u$, or the Joule-Thomson coefficient $(\partial T/\partial p)_h$.

The various kinds of neutral equilibrium can be represented on diagrams in which the lines retain the same order about the point as in Fig. 187 though some are brought into coincidence. For example, if

$$\left(\frac{\Delta T}{\Delta s}\right)_p = 0,$$

it must be possible for the entropy to change along the isopiestic without change in temperature. If pp' in Fig. 187 is rotated clockwise until it coincides with TT' the diagram will represent this condition. If uu' and hh' are not to coincide with pp' and TT' then a decrease in pressure along either uu' or hh' will correspond to a decrease in temperature. This

is the diagram for a two-phase state.

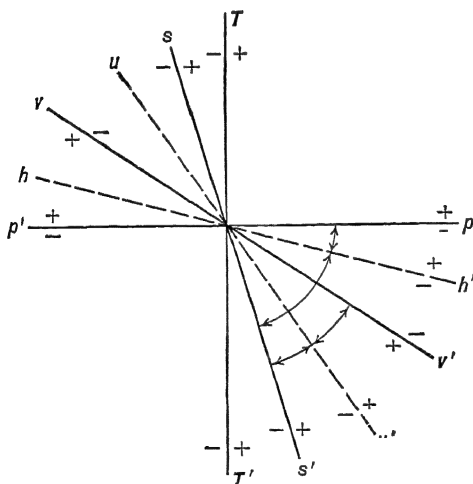


FIG. 188. Arrangement of Lines about a Point for $(\partial p/\partial s)_v < 0$

States for Which $(\partial p/\partial s)_v$ Is Less than Zero

Two classes of states remain to be considered, namely, those for which $(\partial p/\partial s)_v < 0$ and $(\partial p/\partial s)_v = 0$, respectively. By reasoning similar to that given above it can be shown that the order of lines about a point is as in Fig. 188 if $(\partial p/\partial s)_v < 0$ and the substance is stable. This case may be identified with that of liquid water below the temperature of maximum density for which a rise in

temperature at constant pressure results in a decrease in volume $[(\partial v/\partial T)_p < 0]$. It is noteworthy that both the Joule and the Joule-Thomson coefficients are less than zero for a state of this class.

States for Which $(\partial p / \partial s)_v$ Is Equal to Zero

Finally, the class of states for which

$$\left(\frac{\partial p}{\partial s}\right)_v = 0 = -\left(\frac{\partial T}{\partial v}\right)_s$$

is represented by Fig. 189. A state of this sort is a state of maximum or minimum density corresponding to the pressure. It is also a state of maximum or minimum entropy corresponding to the temperature. Therefore, the series of states which marks the left-hand envelope of the p - v diagram also marks either a left-hand or a right-hand envelope of the T - s diagram (Fig. 190).

The Triple Point

A state comprising solid, liquid, and vapor phases at the triple point is a state of neutral equilibrium for which

$$\left(\frac{\Delta p}{\Delta s}\right)_v = 0 = -\left(\frac{\Delta T}{\Delta v}\right)_s,$$

where Δ denotes a finite variation. No change in temperature occurs for reversible adiabatic changes in volume. Any two reversible adiabatics within the region of the triple point when joined by any other pair of reversible processes wholly within that region constitute together a Carnot cycle. Both the net heat and net work of such a cycle must be zero since either positive or negative work in a reversible cycle of this description would violate the Second Law.

The Stability of Phases of a Pure Substance

It was shown in Chapter XIV that *the maximum amount of useful work that a system can produce when it changes between two states in each of which it is in temperature and pressure equilibrium with the same large environment is equal to the decrease in the value of Z for the system.* The useful work was defined as the work in excess of the work done by the system in displacing the environment.

If in a given process the maximum amount of useful work is less than zero, then the process cannot occur without the aid of work which comes

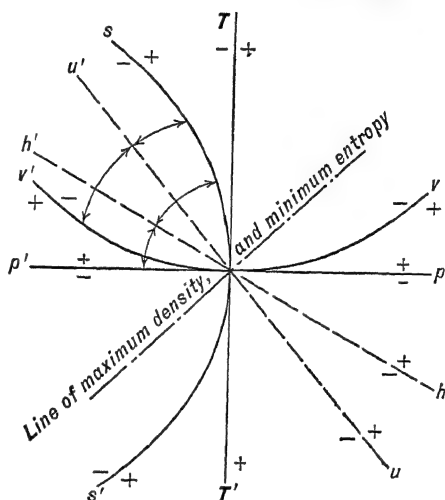


FIG. 189. Arrangement of Lines about a Point for $(\partial p / \partial s)_v = 0$

from some source other than the system or the environment with which it is in equilibrium. If, then, we consider the environment to consist solely of a large and stable medium, no process can occur which involves

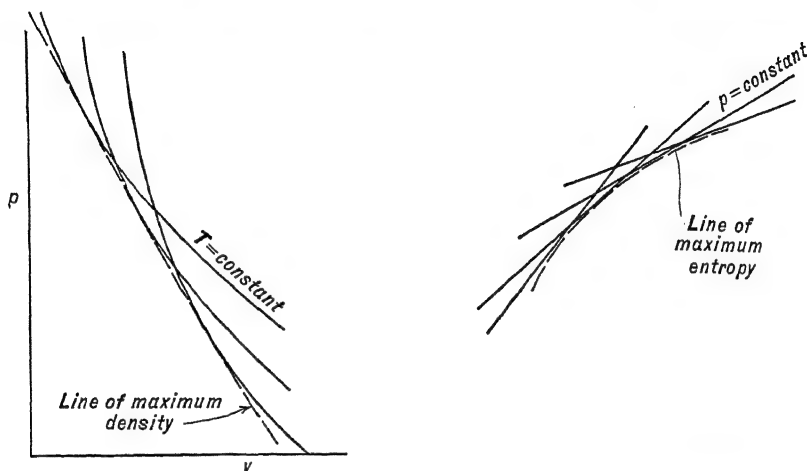


FIG. 190. The Lines of Maximum Density and Maximum Entropy

an increase in the value of Z for the system. Therefore, a system is in a state of stable equilibrium with a stable medium of uniform pressure and temperature if it is in temperature and pressure equilibrium with the medium and if for all possible variations in the state of the system

$$\Delta Z \Big|_{T,1} > 0. \quad [240]$$

This is the fourth criterion of stability given in Chapter XXIII.

Let us apply this criterion to a pure substance for which the equation of van der Waals holds. Isotherms for temperatures greater and less than the critical temperature are represented in Fig. 191 by curves a and b respectively. In curve a there is no distinction between the liquid and vapor phases, but in curve b states to the left of the minimum point M may be called liquid states, and states to the right of the maximum point N may be called vapor states. For any one pressure, such as p' , lying between the pressures corresponding to states M and N there are three states, Q , W , and R , having identical pressures and identical temperatures. In order to determine the relative stability of these three states let us prepare a p - ζ diagram.

The definition of Z gives

$$\zeta = u + pv - Ts,$$

and by differentiation

$$d\zeta = du + p dv + v dp - T ds - s dT.$$

For a pure substance

$$du + p dv - T ds = 0,$$

and along an isotherm

$$s dT = 0.$$

Therefore, we have for an isotherm

$$d\zeta = v dp,$$

and for its slope on a p - ζ diagram

$$\left(\frac{\partial p}{\partial \zeta}\right)_T = \frac{1}{v}.$$

It follows that the slope of an isotherm (Fig. 192) will decrease with increasing volume, the vapor line will have less slope than the liquid line at the same pressure, and the two will cross at some common pressure (JK in Fig. 192).

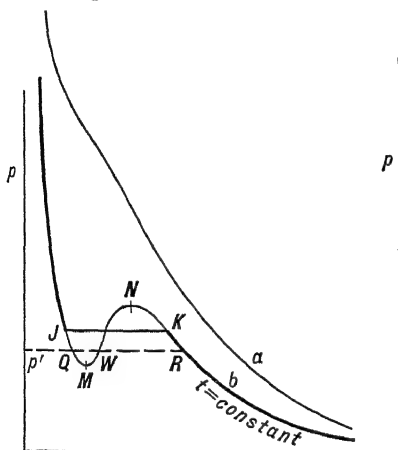


FIG. 191

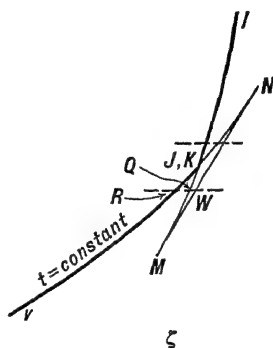


FIG. 192

According to the criterion [240] the line farthest to the left on either side of the intersection will represent stable states, because for any state on the other lines there is a possible variation at constant pressure and temperature of the sort

$$\Delta Z_{T,p} < 0.$$

Thus, the vapor state R is more stable than the liquid state Q , but the liquid state Q is in turn more stable than the state W . On the other side

of the intersection the liquid states will be more stable than the vapor states.

If part of the substance exists in state Q and the remainder in state R the former part will ultimately change to state R , the more stable state. On the other hand, if part is in state J and the remainder in state K it cannot be said that the entire system will ultimately assume either state since the two are equally stable. It follows that when two phases have the same value of Z per unit mass they can coexist in neutral equilibrium.

Vapor in the states represented by the line KN in Fig. 191 is said to be *supersaturated* or *undercooled*, and liquid in the states represented by the line JM is said to be *superheated*. These are called *metastable* states because, as will be shown below, they are stable to all infinitesimal disturbances and to some finite ones. Metastable states of the solid phase are frequently encountered either between a stable solid state and a stable liquid state or between two stable solid states in different solid phases. In many of these cases there is no evidence that the phases are in any sense continuous. Nevertheless, the same criterion applies for coexisting phases.

The state W , which is the least stable of the three states R , Q , and W having the same pressure and temperature, is one for which

$$\left(\frac{\partial p}{\partial v}\right)_T > 0.$$

It is, therefore, a state of unstable equilibrium.

The Primitive and Derived Surfaces of Gibbs

The variation in the energy of a system consisting of a pure substance is given by

$$dU = T dS - p dV, \quad [15]$$

provided that the change of state can be accomplished reversibly in such a manner that $p dV$ is the magnitude of the work done by the system; that is, provided that the system is in an equilibrium state and is uninfluenced by gravity, electricity, capillarity, and magnetism. It follows from [15] that

$$p = -\left(\frac{\partial U}{\partial V}\right)_S \quad [245]$$

and

$$T = \left(\frac{\partial U}{\partial S}\right)_V. \quad [246]$$

Any pair of states to which [15] applies could be represented by two

points in a space whose coordinates are energy, volume, and entropy; and all such states could be represented by a surface in that space. The partial derivatives in [245] and [246] are the slopes of that surface in planes normal respectively to the axis of S and the axis of V . Therefore, a plane tangent to the surface represents quantitatively in the two components of its slope the pressure and the temperature corresponding to the state at the point of tangency. Gibbs showed the utility of the energy-volume-entropy space in discussions of equilibrium. It is a geometrical device which illustrates the requirements for equilibrium of phases and simplifies the solution of many problems relating to the pure substance. We shall refer to this space as the E - V - S space rather than the U - V - S space because we shall wish to represent non-homogeneous states and states involving motion as well as states to which [15] applies.

A surface in the E - V - S space (Fig. 193) representing all possible homogeneous states of a given mass of a pure substance at rest is called a *primitive surface*. If the same mass is in a non-homogeneous state then its energy, volume, and entropy can be found by summing up respectively the energy,

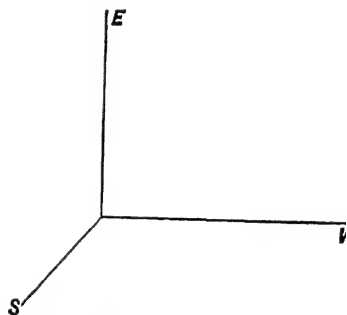


FIG. 193. The E - V - S Space

volume, and entropy of all its parts, which, if small enough, may each be considered homogeneous. Thus a surface can be found in the space which represents equilibrium states including two or more coexisting phases. Such a surface is called a *derived surface*.

The Derived Surface for Coexisting Phases

Since the three coordinates of a non-homogeneous state of a system can each be found by summing up the corresponding values for each part of the system, it follows that the state can be represented by a point which is the center of gravity of masses proportional to the masses of the homogeneous parts each placed at the position corresponding to the state of the part it represents. (That is, the position of each mass would represent the state of the entire system, if its condition were changed to that of one of its parts.) Each of these masses lies in the primitive surface; and the center of gravity lies in the derived surface provided that the non-homogeneous state it represents is an equilibrium state. For example, all possible proportions of saturated liquid and saturated vapor will be represented by a surface which is made up of centers of gravity of pairs of masses placed along the saturated liquid and saturated vapor

lines in the primitive surface. The possible positions of the center of gravity for any one pair of saturation states constitute a straight line joining the pair. Since [15] applies to changes in equilibrium mixtures of phases, a plane with slopes representing the pressure and temperature of the mixture will be tangent to the derived surface along the line joining the pair. The same plane must be tangent to the primitive surface at each end of the line because its slopes are identical with the slopes of the surface at the points of contact.

Tangency of a single plane to the primitive surface at the saturation states of the two phases is equivalent to the condition that ζ must be the same for two coexisting phases (see page 418). For it can be shown from [245] and [246] that the value of the function $(E + pV - TS)$ is identical with the height above the origin at which the tangent plane cuts the axis of E . If this height is the same for two states, as in the case of identical tangent planes, then ζ is the same for both.

The Thermodynamic Surface and Stability

The primitive surface described above represents only homogeneous states of equilibrium, though all need not be states of stable equilibrium. Derived surfaces represent equilibrium states which may be of neutral equilibrium. Any non-equilibrium state is not in general represented by a point on either the primitive surface or a derived surface. For instance a state of a non-homogeneous system, all parts of which are at rest, is represented by the center of gravity of masses, proportional to the masses of the parts, placed at various points on the primitive surface. Since the surface is curved the center of gravity will not in general lie on the surface. The effect of motion of the parts is to raise the masses vertically above the primitive surface by amounts equal respectively to the kinetic energy of the entire system if it is endowed successively with the velocities of the corresponding parts. Thus the point representing the state of a system parts of which are in motion will sink lower in the E - V - S space as the parts come to rest, provided that no other change occurs in their condition.

Consider a system in state E' , V' , S' confined in a cylinder by a piston which is connected with a flywheel. The flywheel is to serve as a "reservoir" of work. The walls of the container which confine the system are to have a thermal conductivity which is small but not zero, and their internal energy and their volume are to remain unaltered by any changes in the system or its surroundings. Now suppose the system and its container to be surrounded by a large and stable medium or atmosphere having a constant pressure p_0 and a constant temperature T_0 .

If the system is not in a state of stable equilibrium a change may occur involving interaction between parts of the system and between the system and the medium until finally the system comes to state E'' , V'' , S'' . During this process, the medium, if it is large enough, will suffer no change in temperature or pressure. Since the medium itself is in a stable and homogeneous state, we may write [15] in the form

$$dE_m = T_m dS_m - p_m dV_m,$$

where symbols with subscript m denote properties of the medium. Integration at constant p_m and T_m gives

$$E''_m - E'_m = T_m(S''_m - S'_m) - p_m(V''_m - V'_m), \quad [a]$$

where the single accent refers to the initial state and the double accent to the final.

The flywheel may absorb energy if it starts from rest, but it cannot deliver a net amount of energy. Therefore

$$E''_m + E'' \leq E'_m + E'. \quad [b]$$

By the principle of the increase of entropy, the sum of the entropies may increase, but cannot diminish, or

$$S''_m + S'' \geq S'_m + S'. \quad [c]$$

Finally, the volume enclosed within the bounds of the medium may be considered unchanged in the process, or

$$V''_m + V'' = V'_m + V'. \quad [d]$$

If these four equations are arranged in the form

$$-E''_m + T_m S''_m - p_m V''_m = -E'_m + T_m S'_m - p_m V'_m,$$

$$E''_m + E'' \leq E'_m + E',$$

$$-T_m S'' - T_m S''_m \leq -T_m S' - T_m S'_m,$$

$$p_m V'' + p_m V''_m = p_m V' + p_m V'_m,$$

by addition we have

$$E'' - T_m S'' + p_m V'' \leq E' - T_m S' + p_m V'. \quad [247]$$

The quantity $T_m S - p_m V$ is the vertical distance between the origin of coordinates and a point at S , V on a plane passing through the origin representing in its inclination the pressure p_m and the temperature T_m . (A plane with this inclination we shall call a p_m - T_m plane.) The two members of the preceding equation, therefore, represent respectively the

vertical distances of the points representing the final and initial states above that plane. (A similar equation could be written for the normal distances, because the normal distance between a point in space and a plane is proportional to the vertical distance between them.)

It follows that any change which can occur in the state of the system surrounded by the medium in question results in a decrease in the height of the state point above the p_m - T_m plane (distances below the plane being considered negative heights). *The most stable state of all the states the system can assume is the one represented by the point in the E - V - S space which is the least distance above (or the greatest distance below) the p_m - T_m plane.*

The sign of inequality in [247] holds, and the initial state is therefore not a stable one, if [b] or [c] is an inequality. Now [b] is an inequality if there is any possibility of delivering work to the flywheel. There is such possibility if, for example, a difference in pressure exists between any part of the system and the surrounding medium or even between different parts of the system. Likewise [c] may be an inequality if, for example, the system, or any part of it, and the medium are initially at different temperatures, or if a part or all of the system is in motion relative to the medium (for an irreversible decrease in velocity of a system, say at constant volume, has the same effect on temperature and entropy as an addition of heat).

Consider the state represented by the point on the primitive surface which is the least distance above the p_m - T_m plane through the origin. Then, if the plane is moved parallel to itself until it is in contact with the primitive surface at that point, it will be tangent to the surface because no point in the surface can be below the plane. Therefore the surface must be concave upward. It follows, too, that the system in this state is at the temperature T_m and the pressure p_m because the inclination of the surface is the same as that of the plane.

Any stable homogeneous state of the system is represented by a point on a surface that is concave upward, and there is no other point on the surface which falls below the plane of tangency passing through this point. Any non-homogeneous state for which all parts are at rest is represented by a point which lies above or on the concave-upward surface of stable states, because this point is the center of gravity of masses placed on the surface. Motion of any part of the system relative to the medium will result in higher E for the same V and S . Therefore the concave-upward surface of stable states is the lower boundary of a solid representing all possible states of the system (there being no upper boundary), and all states of stable equilibrium lie in the boundary surface. The point in this solid which is the least distance above the p_m - T_m plane

passing through the origin lies in the surface and represents a state for which the pressure of the system is p_m and the temperature is T_m . If there is only a single state which is the least distance above this p_m - T_m plane (that is, if there is only one lowest point of tangency to a p_m - T_m plane), then a spontaneous change from this state to any other state is impossible and the point on the primitive surface represents the state of stable equilibrium. The converse, that a change may proceed if the system is in any other state, is also true, and the tendency to change will vanish only when the succession of states reaches the surface of stable states at p_m, T_m .

States of Neutral Equilibrium

If a p_m - T_m plane is tangent to the surface at more than one "lowest" point then the different points of tangency represent equally stable states. By virtue of the tangency, the system in all such states has the pressure and temperature of the medium. If there are two such states then the line joining them in the space diagram represents mixtures of the two in various proportions, and the two states are identified as two phases which can coexist (Fig. 194). At each tangent point the surface is concave upward, so

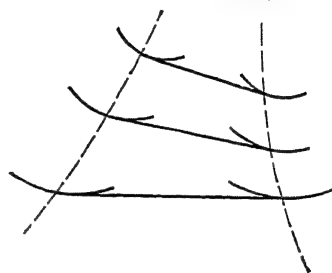


FIG. 194. Lines of Tangency in a Derived Surface

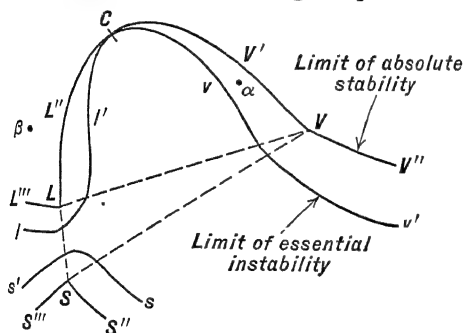


FIG. 195

that a tangent plane can be rolled along the two inverted ridges, taking at each new position a new inclination corresponding to the pressure and temperature of equilibrium for the coexisting phases. The states represented by intermediate points on the line of tangency for any position of the rolling plane are equilibrium states that are not unstable since the concave-upward nature of the surface along the rolling lines makes the surface comprising the lines of tangency concave upward also. That is, there is no point at a lesser distance above the p_m - T_m plane than a point representing a mixture of two phases at p_m and T_m , but there are some points (i.e., others along the line of tangency) which are equally distant. Therefore the state of the mixture is a state of neutral equilibrium.

At the triple point a single plane is tangent to the primitive surface at three points, namely, the points representing the saturation states of the solid, liquid, and vapor phases respectively (Fig. 195). The plane triangle bounded by the straight lines joining the three states includes points representing all possible equilibrium combinations of the three phases. The common tangent plane which touches the primitive surface at S , L , and V (Fig. 195) can be rolled along a pair of ridges in any one of three directions. It can lift at S and roll along the lines LL'' representing states of the saturated liquid and VV' representing states of the vapor which can coexist with them. It can lift at L or at V and roll along lines representing other pairs of states which can coexist in equilibrium. When the critical point C is reached the two lines of contact join and the rolling of the plane ends.

States of Unstable and Metastable Equilibrium

Beyond the critical point the liquid and vapor phases are continuous. It is reasonable to assume that the continuity exists below the critical point and that the primitive surface (the surface representing homogeneous states) continues uninterrupted from liquid side to vapor side. It will be recalled that the equation of state of van der Waals represents a continuity of this kind.

For homogeneous states the pressure is not fixed by the temperature; therefore, the primitive surface between the liquid line LC and the vapor line VC will not coincide with the derived surface which represents two-phase states. It must lie above the derived surface because that surface was so constructed that no states can lie below it. Since the primitive surface outside the boundaries $LL''CV'V$ is everywhere concave upward and the part of the primitive surface between LL'' and VV' is entirely above a plane tangent at both boundaries, it follows that some part of the primitive surface between the boundaries is convex upward if the surface is continuous.

This reversal of curvature indicates states of unstable equilibrium. For a tangent plane (which still represents the pressure and temperature) will lie above all the points representing neighboring states, and it was shown above that any process may occur which results in a decrease in the height of the state point above the pressure-temperature plane of the medium. Even if the substance in one such state were in complete pressure and temperature equilibrium with its environment, the equilibrium would be unstable because any disturbance of either pressure or temperature, however slight, would cause a sweeping change toward a state lower in the space (relative to a p_m - T_m plane) and more stable. The locus of the points of inflection which mark the reversal in curvature

is shown on Fig. 195 as line $U'Cvv'$. Gibbs calls it the "limit of essential instability." The saturation curves $L'''LL'CV'VV''$ and $S'''SS''$ he calls the "limit of absolute stability."

No state which lies within the limit of essential instability will ever exist long enough to be observed as a homogeneous state. But states which lie between essential instability and absolute stability are often encountered. The surface representing these states is concave upward, but a plane tangent to the surface will intersect the primitive surface elsewhere. The height above a p_m - T_m plane is less for the state at the point of tangency than for all neighboring states but may be still less for some state for which the values of E , V , S , and other properties are different by a finite amount. A system in such a state would be stable to all infinitesimal disturbances and to some small finite ones, but a disturbance greater than a certain magnitude will cause the state of the system to sweep to a condition of absolute stability. Any state which lies between essential instability and absolute stability is a metastable state.

An example of a metastable state is afforded by liquid water which has been cooled below the freezing temperature. This is called a *supercooled liquid*. A crystal of ice bigger than a certain finite size will probably cause immediate solidification of at least part of the system. Liquid water that has been carefully freed of dissolved air may be heated to a temperature above the normal boiling temperature without the formation of vapor. A liquid whose temperature is higher than its normal temperature of boiling is called a *superheated liquid*; and a vapor whose temperature is less than its normal temperature of condensation is called a *supersaturated vapor* or an *undercooled vapor*. Either of these is in every respect a continuation inside the limit of absolute stability of the normal single-phase conditions.

The stability of a supersaturated vapor to small disturbances is shown by the fact that a tiny (but not infinitesimal) drop of water introduced into it will not grow but will evaporate. However, a supersaturated vapor will condense on a drop larger than a certain size. (A superheated liquid will evaporate into a bubble larger than a certain size, but bubbles smaller than that size will condense.) The state of a supersaturated system in equilibrium with an environment at p_m , T_m is represented by a point such as α on the primitive surface in Fig. 195. The stable state which this system will attain if subjected to a large enough disturbance is represented in the figure by point β on the primitive surface. The tangent planes at α and β are parallel planes with the inclination p_m , T_m ; but the tangent plane at α cuts the primitive surface, whereas that at β lies wholly below it.

It is possible that between certain phases no limit of essential instability can be found. For example, a liquid may be cooled below its freezing point, and as the temperature is lowered the viscosity increases continuously until, under some circumstances, it becomes so large that the system behaves as a solid in most respects. A supercooled liquid of indefinitely large viscosity is called a *glass*. Glasses in general can be cooled to the absolute zero of temperature without changing to a more stable crystalline solid state. It must be concluded, therefore, that the primitive surface is in many cases discontinuous between liquid and solid phases.

The Thermodynamic Surface and Availability

Gibbs defines and describes in terms of the E - V - S space the *available energy of the system*, its *capacity for entropy*, and several other quantities. Of these the one of greatest practical importance appears to be what he has called the *available energy of the system and medium*. It can be defined as the maximum work which can be delivered to things other than the system and medium by the two when unaided by any changes (except cyclic changes) in any external things. Gibbs states that it is equal to the vertical height of the state point in the E - V - S space above a p_m - T_m plane which is tangent to the surface of stable states (that is, tangent at the lowest point of tangency). It can be shown with the aid of [245] and [246] that this distance is given by

$$(E + p_o V - T_o S) - (E_o + p_o V_o - T_o S_o), \quad [145]$$

where subscript o refers to the state of the system corresponding to the point of tangency. It follows that

$$p_o = p_m$$

and

$$T_o = T_m.$$

Reference to Chapter XVII will show that the available energy of the system and medium as defined by Gibbs is identical with the quantity that we have called *availability*. When it is interpreted in terms of the E - V - S space it becomes a measure of stability of the system in the presence of the medium. In fact, the system is in its most stable state when the availability as given by [145] is zero.

PROBLEMS

1. Using a fluid having the van der Waals equation of state, give examples of states of stable equilibrium, neutral, metastable, and unstable equilibrium. Justify each example.

2. (a) Tabulate all the facts that you can deduce from Fig. 187 concerning partial derivatives of properties of a substance for which $(\partial p / \partial s)_v > 0$.

- (b) Do the same for a substance for which $(\partial p/\partial s)_v < 0$, using Fig. 188.
- (c) Do the same for a fluid at a condition of maximum density, using Fig. 189.
3. Starting from the conditions for stability of a pure substance, show that the order of lines about a point are (a) as in Fig. 188 if $(\partial p/\partial s)_v < 0$, and (b) as in Fig. 189 if $(\partial p/\partial s)_v = 0$.
4. Find the order of lines about a point for each of the kinds of neutral equilibrium listed in the footnote on page 411.
5. Starting from saturation data from the *Steam Tables* and Bridgman's p - v - T data for liquid water, develop p - v and T - s charts for states on either side of the line of maximum density. See Bridgman, *The Physics of High Pressures*, Macmillan, 1931, p. 143.
6. Plot the isotherms corresponding to 1000 F, the critical temperature, and 212 F for H_2O on a p - ξ diagram. On the same diagram, plot the curve of saturation states. By extrapolation show the curves of metastable states.
7. Show by the most direct method that if the values of ζ at J and K in Fig. 191 are identical then the area $JMNKJ$ on the p - v diagram must be zero.
8. (a) Show that the volume and entropy of a system are given by the inclinations of a plane tangent to the surface of most stable states in a Z - p - T space.
- (b) What other properties can be shown by the inclinations of tangent planes to surfaces of stable states in three-dimensional diagrams?
9. Prove that a non-homogeneous state can be represented in the E - V - S space by the center of gravity of masses proportional to the masses of the homogeneous parts if each mass is placed in a position which would represent the state of the entire system if its condition were changed to that of the part.
10. Show that (a) the value of the function $(E + pV - TS)$ is identical with the height above the origin at which a tangent plane at the state E, V, S on the primitive surface cuts the axis of E ; (b) the value of the function $(E + p_oV - T_oS)$ is the vertical height of the state point E, V, S above a p_o - T_o plane which passes through the origin; (c) the value of the function $[(E + p_oV - T_oS) - (E_o + p_oV_o - T_oS_o)]$ is the vertical height of the state point E, V, S above a plane which is tangent to the primitive surface at the state point E_o, V_o, S_o .
11. Using data from the *Steam Tables*, (a) plot on a u - s diagram the traces of the surface of most stable states in the E - V - S space on planes for which the volume is 0.05, 0.5, and 5 ft³/lb; (b) plot on a u - v diagram the traces of the surface on planes for which the entropy is 1, 1.3, and 1.6 Btu/F lb. (c) Show on these diagrams the projections of the line of saturation states. (d) Select a single state and show graphically the pressure and temperature corresponding to it. (e) Show graphically the availability for some other state as regards a medium at the pressure and temperature of (d). (f) Sketch the probable course of the lines of metastable states for the volumes and entropies given above.

SYMBOLS

- c_p specific heat at constant pressure
 E internal energy of a system

p	pressure
s	entropy per unit mass
S	entropy
T	absolute temperature
u	internal energy of a unit system in the absence of motion, gravity, etc.
U	internal energy of a system in the absence of motion, gravity, etc.
v	specific volume
V	volume

GREEK LETTERS

δ	a variation as specified
Δ	a variation of any order, finite or infinitesimal
ζ	$(u + pv - Ts)$
Z	$(E + pV - TS)$

SUBSCRIPTS

h	constant enthalpy
m	medium
o	point of tangency
p	constant pressure
s	constant entropy
T	constant temperature
u	constant internal energy
v	constant volume

SUPERSCRIPTS

'	initial state
"	final state

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CHAPTER XXV

SUPERSATURATED VAPOR AND SUPERHEATED LIQUID

Experimental Evidence of Metastable States

Ample evidence is available that metastable states of the vapor and liquid phases exist commonly and under circumstances that make them of considerable importance in science and engineering. In 1897 C. T. R. Wilson* published an account of the behavior of water vapor mixed with air and other gases when subjected to rapid expansion. He showed that dust-free air saturated with water vapor can be expanded isentropically to a volume 25 per cent greater before condensation occurs, whereas according to Dalton's Law for stable mixtures condensation should begin with the expansion.

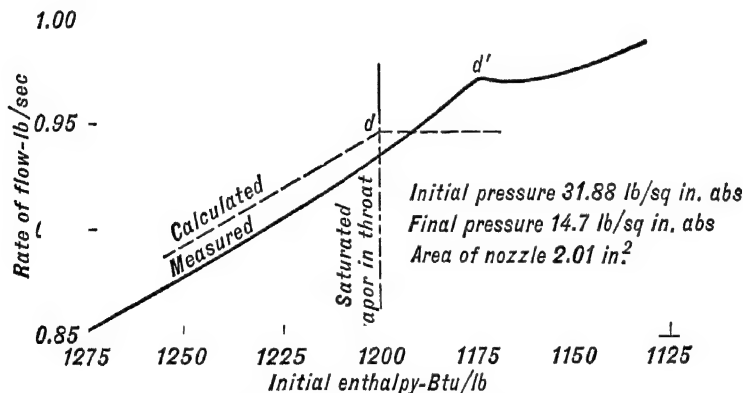


FIG. 196. The Discharge from a Converging Nozzle with Expansion Crossing the Saturation Line

Measurements made by the Department of Steam-Turbine Engineering of the General Electric Company. Reproduced by courtesy of the General Electric Company.

The flow of steam through a frictionless, adiabatic nozzle for different initial temperatures while the initial and final pressures are held constant can be computed from *Steam Table* data if the steam assumes only stable equilibrium states. The result of such a computation is shown by the dash line in Fig. 196 in which the discontinuity d occurs at the

* *Phil. Trans., A*, Vol. 189 (1897), pp. 265-307.

Wilson's interest in the "cloud chamber" arose from the fact that charged particles (α -rays, x-rays, etc.) cause ionization of the gas which in turn promotes condensation. The liquid particles that form make the track of the particles evident.

highest initial superheat at which the liquid phase appears at the throat of the nozzle. The measured flow, on the other hand, follows the solid line which at higher superheats parallels and, because of friction, falls slightly below the computed values. The discontinuity on the measured curve, d' , occurs at a lower initial superheat than on the computed curve. The course of the measured curve between d and d' and the excess of the measured flow over the computed value at low superheats both suggest that condensation fails to occur even when the state of the vapor passes appreciably beyond the saturation state.

The condensation of supersaturated vapor has been observed visually by Yellott* and others. A two-dimensional nozzle with glass walls is illuminated by a light beam directed along the length of the jet. A search tube, t , Fig. 197, samples the static pressure of the stream through

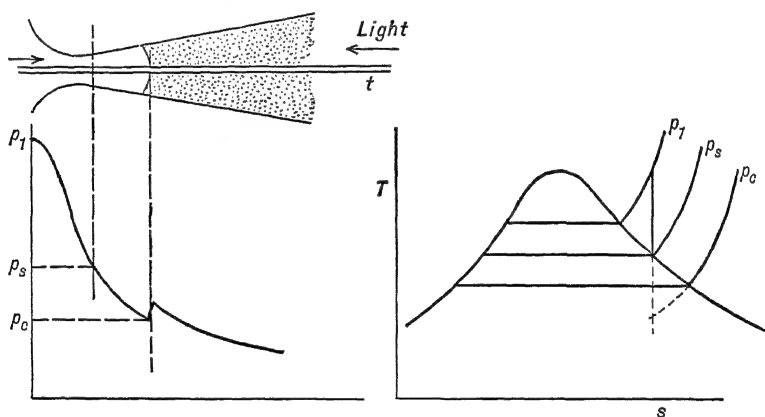


FIG. 197

a small hole in the wall of the tube so that the course of the pressure along the stream can be plotted as shown. If the steam is brought to the nozzle in a superheated state, expansion occurs without visible trace of liquid through the saturation state at p_s and to a state at a considerably lower pressure p_e where a fog of liquid particles is formed. The diameter of each of the particles of fog is probably less than a wave length of visible light because only a blue haze, typical of light scattered by particles of such dimensions, is visible. At the point of condensation a discontinuity occurs in the course of the pressure in the stream.

Less extensive but equally convincing evidence is available of the existence of metastable liquid states. At any finite temperature a stable

* Yellott and Holland, *Trans. A.S.M.E.*, Vol. 59 (1937), pp. 171-183; Yellott, *ibid.*, Vol. 56 (1934), pp. 411-430; Rettaliata, *ibid.*, Vol. 58 (1936), pp. 599-606.

liquid will vaporize before the pressure it exerts on its container reaches zero. But it is well known that liquid water free from dissolved gases will cause the inward collapse of the walls of a thin glass container if it is cooled carefully. The collapse is the result of tension or *negative pressure* in the liquid. If the walls of the container do not fail, the liquid may be maintained in a condition of tension indefinitely, though a sudden blow on the walls may result in vaporization and the establishment of the saturation pressure corresponding to the stable two-phase state. A small amount of air coming out of solution will have the same effect.

A direct measurement of a negative pressure can be made by connecting a container full of warm, air-free liquid with a mercury manometer through a liquid-filled capillary tube as shown in Fig. 198. If the

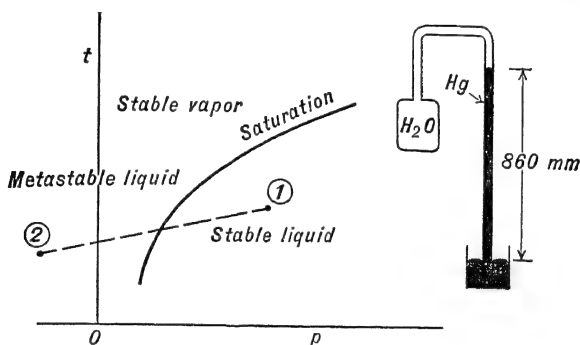


FIG. 198. Cooling Liquid Water to Negative Pressure

liquid in the container is carefully cooled the column of mercury will rise to as much as 100 mm in excess of the barometric height.* The change of state of the liquid in this case is illustrated in Fig. 198 where point 1 represents the stable state of the warm liquid and point 2, on the same line of constant volume projected beyond the stable region, represents the metastable state of the liquid under negative pressure or tension. Of course, negative pressure is not a necessary condition for a superheated liquid since any state of the liquid represented by a point in Fig. 198 to the left of the saturation line is either a metastable state or an unstable state.

If hot liquid water is expanded adiabatically and reversibly through a nozzle to a lower pressure the rate of flow can be computed from *Steam Table* data in precisely the same fashion as the rate of flow of

* Worthington (*Proc. Roy. Soc., A*, Vol. 50 (1892), pp. 423-424) observed ethyl alcohol at a pressure of -250 lb/sq in.

vapor. Until the end of the expansion reaches the line of the saturated liquid (at p_s , Fig. 199) very little increase in volume occurs between inlet and discharge. But once the saturation line is crossed the forma-

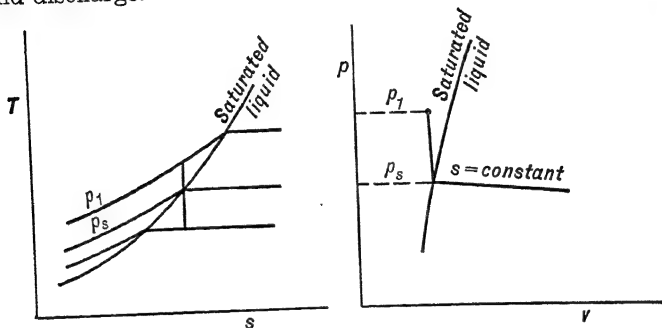


FIG. 199

tion of vapor greatly increases the specific volume of the fluid and correspondingly restricts the calculated rate of flow (Fig. 200). Measurements have been made,* however, which indicate rates of flow

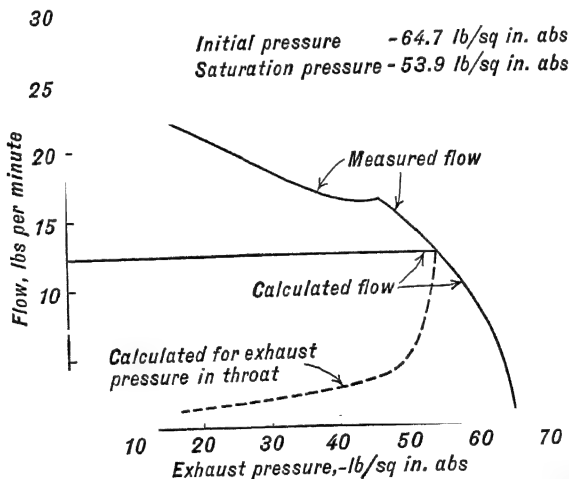


FIG. 200. Calculated and Measured Flow of Hot Water through a $\frac{1}{8}$ -inch Diameter Converging Nozzle

From J. L. Danforth, M. S. Thesis, M. I. T., 1941.

through nozzles as much as five times the computed flow, which can be explained only on the hypothesis that vaporization does not occur when

* W. T. Bottomley, *Trans. North East Coast Inst. of Engineers and Shipbuilders*, Vol. 53 (1937), pp. 65-92.

J. L. Danforth, M. S. thesis, M.I.T., 1941.

the pressure is lowered to the pressure of vaporization. Visual observation of the flow of liquid water through a glass nozzle has confirmed this hypothesis.

Methods of Determining Properties for Metastable States

The properties of a system in a metastable state cannot be measured readily because such a state usually will not endure the disturbance incident to measurement. Thus a thermometer exposed to a stream of supersaturated vapor will serve as a nucleus for condensation and will take up a temperature other than that of the surrounding vapor.

In the absence of measurements the properties of metastable states can be found by extrapolating the properties of stable states, because

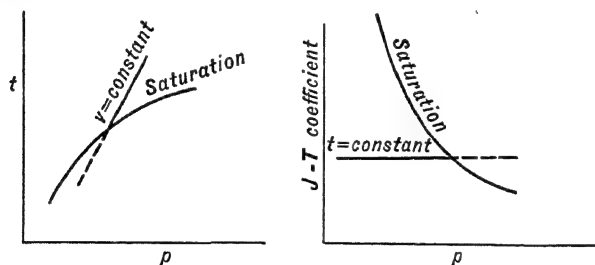


FIG. 201. Extrapolation of Lines of Constant Volume and Constant Temperature into the Region of Supersaturated Vapor

the metastable region is merely the extension of a stable phase beyond the limit of absolute stability. For example, if the pressure-volume product is virtually constant along an isotherm in the vapor phase the specific volume corresponding to any metastable state of the vapor at the same temperature can be found from the constant of the stable region. Similarly, if the specific volume is virtually constant along an isotherm in the liquid phase the specific volume corresponding to any metastable state of the liquid at the same temperature is the same as that for stable states.

Again, if an isentropic expansion in the vapor phase corresponds to the pressure-volume relation

$$pv^k = \text{constant},$$

the same equation with the same constant and the same exponent will represent the relation when the expansion has crossed the saturation line into the metastable region.

In the precise determination of the properties of a supersaturated vapor it is well to choose for extrapolation those measured values which together form a nearly linear relation as the saturation line is approached.

For example, the pressure-temperature relation along an isometric, Fig. 201, and the Joule-Thomson coefficient along an isotherm are easy to extrapolate.

Disturbances Necessary to Cause Change to a Stable State

Consider a central piece of a large mass of fluid in a metastable state. If a change to a more stable state is to occur the change must be initiated by the formation of a minute amount of the more stable phase within the mass. That is, the change toward stability must begin with the formation of a tiny drop in a supersaturated vapor or of a tiny bubble in a superheated liquid. But since a metastable state is one which will persist despite infinitesimal disturbances a sufficiently small drop will not cause condensation of a supersaturated vapor but will itself evaporate, and a sufficiently small bubble will not cause evaporation of a superheated liquid but will itself condense. On the other hand, if the vapor is exposed to a large surface of liquid it will condense on it and the amount of liquid present will increase; similarly superheated liquid will evaporate into a large space filled with vapor. It remains to determine how large a mass of liquid is necessary to initiate condensation, or how large a mass of vapor is necessary to initiate vaporization in a metastable fluid.

Equilibrium between Phases at a Curved Surface

As regards interaction with surrounding vapor, the difference between a minute drop and a large mass of liquid is the curvature of the surface which the liquid presents to the vapor. Lord Kelvin* and R. von Helmholtz† have shown that the curvature of the surface of separation between two phases determines the equilibrium pressure for coexistence of the two at any temperature. The method of analysis is as follows:

Consider a system consisting of a liquid and its vapor in stable equilibrium in a gravitational field of standard acceleration g_0 . For stability under such circumstances the temperature must be uniform despite the hydrostatic variations in pressure. Let a capillary tube of a material that the liquid will not wet be placed vertically in the liquid. Within the tube the liquid-vapor boundary is a curved surface which is depressed a distance y' (Fig. 202) below the flat boundary surface outside the tube. Because of hydrostatic forces the vapor in the tube below the flat surface is at a pressure exceeding that of the vapor in equilibrium with the flat surface at the same temperature. If the pressure of equilibrium is

* *Proc. Roy. Soc. Edin.*, Vol. VII (1870), p. 63; also *Phil. Mag.* 4th Vol. 42 (1871), pp. 448-452.

† *Wied. Ann.*, Vol. 27 (1886), pp. 508-543.

the same for the curved surface in the capillary as for the flat surface outside, then vapor must condense on the curved surface and a flow will occur down the tube.

Now if a turbine wheel is introduced into the entrance to the tube some work may be delivered by the system, because any drop in pressure across the wheel less than the hydrostatic head of vapor corresponding to y' will not prevent circulation of the fluid. If a heat source sufficiently

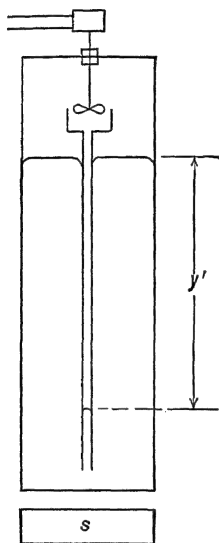


FIG. 202

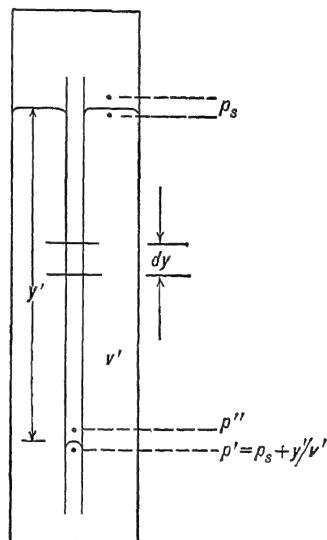


FIG. 203

Equilibrium of a Vapor with a Curved Surface of Liquid

high in temperature provides a compensating flow of heat, the work taken out will cause no change in the energy of the system and the operation can be made continuous. But this device is a perpetual-motion machine of the second kind. Therefore, the vapor and the liquid must be in equilibrium at the curved surface, and the vapor in the capillary between the level of the flat surface and that of the curved surface is supersaturated vapor.

If the curvature of the surface is of radius r and the surface tension is σ the surface exerts a downward force on the liquid below it of magnitude $2\pi r\sigma$. For dynamic equilibrium of an element of fluid immediately below the surface we may write

$$\pi r^2 p'' + 2\pi r\sigma = \pi r^2 \left(p_s + \frac{y'}{v'} \right);$$

where p_s denotes the pressure of the vapor on the flat surface, p'' its pressure on the curved surface, and v' the mean volume of unit weight of the liquid over the height y' (Fig. 203). Since p'' exceeds p_s only by the hydrostatic head of vapor the difference ($p'' - p_s$) can be neglected, except near the critical state, as compared with the hydrostatic head of the liquid y'/v' . Then

$$2\pi r\sigma = \pi r^2 \frac{y'}{v'}$$

or

$$y' = \frac{2\sigma v'}{r}. \quad [248]$$

The equilibrium pressure of the vapor corresponding to the liquid surface of radius r exceeds that corresponding to the flat surface by the hydrostatic head of vapor over the height y' . For an element of vapor in the capillary of depth dy pressure equilibrium is expressed by

$$\frac{dy}{v} = dp,$$

where v denotes the volume of unit weight of the vapor. Since the temperature of the system is uniform we may write for low pressures

$$pv = \text{constant} = p_s v_g,$$

where v_g is the specific volume of the saturated vapor over the flat liquid surface. Substitution in the preceding equation gives

$$\frac{dp}{p} = \frac{dy}{p_s v_g}.$$

Integrating between $y = 0$ and $y = y'$ we get

$$\ln \frac{p'}{p_s} = \frac{y'}{p_s v_g},$$

which upon substitution of the value for y' in [248] gives

$$\ln \frac{p''}{p_s} = \frac{2\sigma}{p_s r} \frac{v'}{v_g}. \quad [249]$$

If the pressure is low enough

$$p_s v_g = RT,$$

and

$$\ln \frac{p''}{p_s} = \frac{2\sigma v'}{rRT}. \quad [250]$$

It follows that for equilibrium between two phases of a pure substance the relation between the temperature and the pressure of the vapor is not unique but is different for different curvatures of the surface separating the phases. In mathematical terms

$$p'' = f(T, r).$$

This relation is shown in Fig. 204, where the solid curve is the saturation line for a flat surface ($r = \infty$) and the dash lines below it are saturation lines for convex liquid surfaces of various radii.

The von Helmholtz analysis is equally valid if the liquid wets the tube and rises to a concave liquid surface for which the sign of the radius

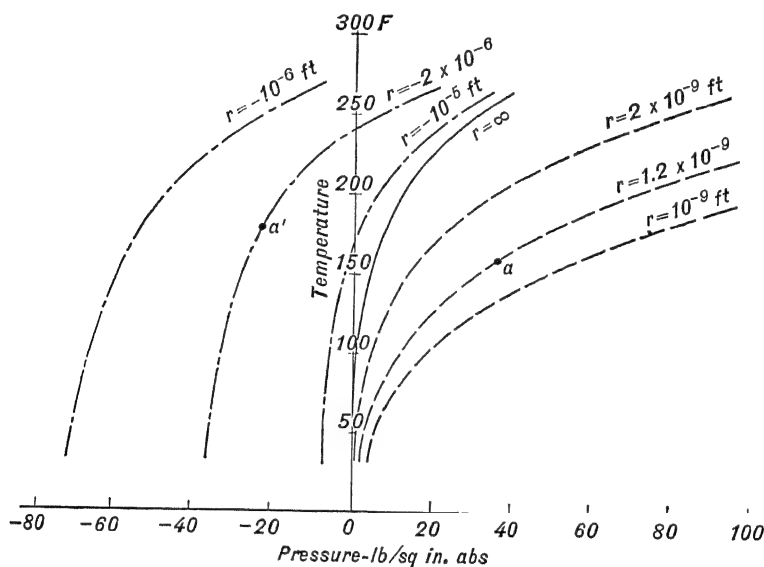


Fig. 204. Equilibrium between Liquid and Vapor at a Curved Surface

Dash lines give pressure of vapor in equilibrium with drops of radius indicated. Dot and dash lines give pressure of liquid in equilibrium with bubbles of radius indicated.

in the analysis given above is changed. The corresponding saturation lines are shown in Fig. 204 as dot and dash lines above the normal saturation line. For these the abscissa represents the pressure of the liquid just below the surface. The liquid in the capillary at levels between the flat surface and the curved surface is at pressures lower than the normal saturation pressure. It is superheated liquid.

Unstable Equilibrium between a Drop and Surrounding Vapor

Though the curved liquid surface of Fig. 202 is in stable equilibrium with the vapor above it, a drop of liquid having a surface of the same

degree of curvature would be in unstable equilibrium with the vapor, for there is no tendency for the drop to grow or to get smaller, but if the drop by some accidental condensation becomes slightly larger it will continue to grow by condensation. Consider, for example, a supersaturated vapor in state a (Fig. 204) in equilibrium with drops of the radius indicated by the dash line passing through a . An accidental condensation on a drop will cause its radius to increase, so that the curve of equilibrium for this drop is moved to the left of point a . Therefore, vapor in state a is at a temperature lower than the equilibrium temperature corresponding to its pressure, and it will condense on the drop. Thus, the drop will continue to grow until its radius of curvature becomes infinite, or until all the vapor is condensed.

Similarly, if the drop should by some accidental evaporation get smaller the curve of equilibrium will be to the right of point a , the vapor will be superheated relative to the drop, and the drop will continue to evaporate.

Therefore the radius corresponding to the saturation curve passing through the supersaturated state a is the radius of the smallest drop of liquid which would grow by condensation when exposed to vapor in state a ; it is also the radius of the largest drop of liquid which would evaporate under the same conditions. The radius corresponding to the saturation curve passing through the superheated liquid state a' has a similar significance with respect to the size of bubbles of vapor.

The Supersaturation Limit

Wilson's tests with the cloud chamber indicate that dust-free air saturated with water vapor can be expanded in volume by 25 per cent before any liquid forms in a reversible and adiabatic process. At this stage a rain of fine drops appears. If the mixture is expanded by 38 per cent a dense fine fog is formed. Using Dalton's law of partial pressures Wilson computed the corresponding *supersaturation ratios*, (the partial pressure of the water vapor divided by the normal saturation pressure corresponding to the temperature) and found them to be respectively 4.2 and 7.9. The corresponding minimum radii of drops that would grow are respectively 8.6×10^{-8} cm and 6.4×10^{-8} cm, according to the Kelvin-Helmholtz equation.

It is doubtful whether these figures represent limits to the supersaturated states of water vapor in the absence of air and other gases. There are available, however, a number of excellent observations* of water vapor in isentropic expansion which show a well-defined limit. Yellott and Holland find that the locus of supersaturated states at

* Refer to footnote on page 430.

which a dense fog of minute liquid particles forms in a nozzle is a line on the Mollier diagram approximately paralleling the saturation line and lying about 60 Btu/lb below it. In the h - s diagram of Fig. 205 the line VV represents the normal saturated vapor, pp a line of constant pressure for metastable (supersaturated) states of the vapor, and pp' a line of constant pressure for equilibrium between phases at boundary surfaces of large radius. Now if an isentropic expansion through a nozzle with smooth walls begins at a superheated state A , it proceeds without formation of liquid until the state B is reached. At state B a mist or haze made up of minute liquid particles forms suddenly. The state B is called the supersaturation limit of the expansion. The line

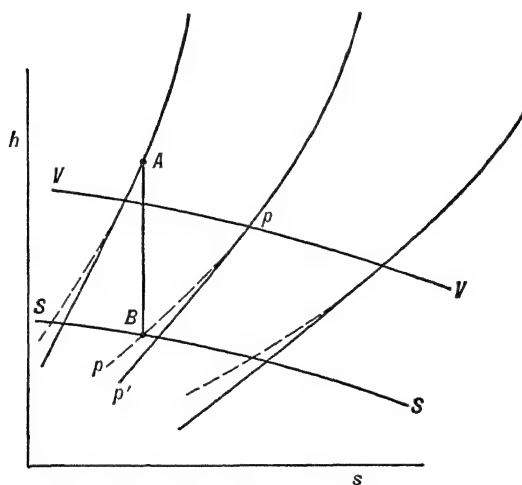


FIG. 205. The Limit of Supersaturation

SS is the locus of points B representing the supersaturation limit for expansion along various isentropics.

From the Kelvin-Helmholtz equation [250] and the curve of the supersaturation limit (SS) the radius of curvature can be computed for the smallest liquid particle that would grow to form a particle of fog. It is found to vary from about 1.4×10^{-9} ft at the lowest pressures investigated (6 lb/sq in. abs) to about 1.7×10^{-9} ft at the highest pressures (40 lb/sq in. abs). It is shown below that a drop of radius 1.4×10^{-9} ft contains about 12 molecules. It is doubtful whether the Kelvin-Helmholtz equation is even approximately valid for radii of this magnitude, but it offers evidence that supersaturation will persist until a small group of molecules, perhaps accidentally assembled, begins to grow.

The Nucleus of Condensation

In their experiments on the flow of steam through nozzles Yellott and Holland have shown that at some point in the course of the expansion a fog is formed suddenly which is visible, when properly illuminated, as a bluish haze. Presumably, there are present in the steam before condensation begins particles of fluid just large enough to grow when exposed to the supersaturated vapor at the point of condensation. The Kelvin-Helmholtz equation permits us to calculate in terms of the surface tension of the liquid the size of the particles that would grow. As one example, Yellott and Holland find a supersaturation ratio (pressure of the vapor divided by the normal saturation pressure corresponding to the temperature) of 5.6 when the temperature of the vapor is 150 F immediately before the point of condensation. If we choose for the surface tension its value corresponding to a flat surface ($p' - p'' = 0$) at 150 F we get for the radius of the drop which begins to grow

$$r = \frac{\sigma_m'}{p_s v_g \ln \frac{p'}{p''}} = \frac{2 \times .0042 \times .015}{3.718 \times 144 \times 97.07 \times \ln 5.6} = 1.4 \times 10^{-9} \text{ ft.}$$

Let us compute the number of molecules comprised in such a drop. A gram mole of H_2O has a mass of 18 grams and contains 6.06×10^{23} molecules. One molecule, therefore, has a mass of 3×10^{-23} gram or 6.5×10^{-26} pound. The mass of a drop of water of radius 1.4×10^{-9} foot and of specific volume $0.014 \text{ ft}^3/\text{lb}$ is 0.8×10^{-24} pound, and it comprises $8 \div 0.65$ or 12 molecules.

Now a drop comprising twelve molecules is a minute drop, but it is unlikely that the vapor phase of water contains molecular groups of this magnitude in such numbers as to cause the formation of the dense fog observed in the nozzle. However, in computing the size of this drop it was assumed that the surface tension is the same as that for a flat surface. A correction of this assumption may be attempted with the aid of [333] which is derived in Chapter XXVI. This equation gives the rate of change at constant temperature of the surface tension σ with the difference between the pressure inside and outside the drop ($p' - p''$):

$$\left[\frac{\partial \sigma}{\partial (p' - p'')} \right]_T = - \frac{m}{F(1/v' - 1/v'')}, \quad [333]$$

where m denotes the mass of the film, F its area, v' the specific volume of the liquid, and v'' that of the vapor. If we assume the density of fluid in the film to be the same as in the liquid, the right-hand member

of [333], which is approximately $(-mv'/F)$, is the negative of the thickness of the film.

The thickness of the film cannot be less than zero, and [333] indicates, therefore, that the surface tension decreases with the radius of the drop. From the Kelvin-Helmholtz relation

$$r = \frac{2\sigma v'}{p_s v_g} \ln \frac{p''}{p_s} \quad [249]$$

it can be seen that, if the value of σ employed is greater than the true value, the value of r is also greater than the true value. That is, the true value of r is probably less than 1.4×10^{-9} foot, and the drop probably contains fewer than twelve molecules.

Let us assume the film to be a single layer of molecules. Then its thickness would correspond to the diameter of a single molecule, which, according to the method used above, proves to be approximately 10^{-9} foot. Substituting this value for the right-hand member of [333] and integrating between $(p' - p'') = 0$ and $(p' - p'')$, we get

$$\sigma = \sigma_1 - (p' - p'') \times 10^{-9}, \quad [251]$$

where σ denotes the surface tension of the drop corresponding to $(p' - p'')$ and σ_1 the surface tension of a flat surface $(p' - p'' = 0)$ at the same temperature. The pressure difference $(p' - p'')$ is balanced by the surface tension, so that

$$p' - p'' = \frac{2\pi r \sigma}{\pi r^2} = \frac{2\sigma}{r}. \quad [252]$$

Therefore, [251] becomes

$$\sigma = \sigma_1 - \frac{2\sigma}{r \times 10^9},$$

or

$$\sigma = \frac{\sigma_1}{1 + \frac{2}{r \times 10^9}}$$

Substitution of this expression for σ in the Kelvin-Helmholtz equation gives

$$\ln \frac{p''}{p_s} = \frac{2\sigma_1 v'}{p_s v_g (r + 2 \times 10^{-9})}.$$

Using the same data for the supersaturation limit as before, we get

$$r + 2 \times 10^{-9} = 1.4 \times 10^{-9} \text{ ft}$$

or

$$r = -0.6 \times 10^{-9} \text{ ft,}$$

a result which indicates by its sign that the assumed effect of pressure on the surface tension is too large. Nevertheless, it is clear from these calculations that some reasonable value for the pressure coefficient of the surface tension will indicate that water particles of the order of magnitude of less than ten molecules will begin to grow at the point where condensation is observed. It is probable that chance groupings of two or more molecules are the nuclei for condensation in the nozzle.

Behavior of a Stream if Large Drops Are Formed

The behavior of the stream of fluid at the point of condensation can be studied in terms of the equations of steady flow. Assume that line c in the nozzle of Fig. 206 represents the plane in which condensation suddenly occurs, so that to the left of c the fluid is transparent and to the right a fog is visible. Assume further that fluid to the left of c is vapor (supersaturated vapor) and that to the right is an equilibrium mixture of vapor and drops of liquid. Let subscript 1 refer to the state of the fluid just to the left of c and let subscript 2 refer to that just to the right of c . For these two sections, if they are very close together, we may write the continuity equation [9],

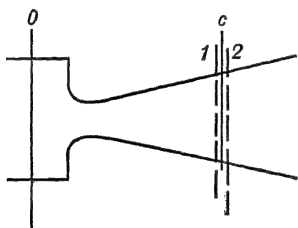


FIG. 206

$$\frac{V_1}{v_1} = \frac{V_2}{v_2},$$

where V denotes the velocity of the fluid and v its specific volume; the energy equation [6],

$$h_1 + \frac{V_1^2}{2g} = h_2 + \frac{V_2^2}{2g} = h_0; \quad [253]$$

and the momentum equation [60],

$$p_1 a_1 + \frac{w}{g} V_1 = p_2 a_2 + \frac{w}{g} V_2, \quad [254]$$

or, since $a_1 = a_2$,

$$p_1 + \frac{V_1^2}{v_1 g} = p_2 + \frac{V_2^2}{v_2 g}. \quad [255]$$

If the state of the fluid is known at some section of large area before the

nozzle (section 0) and the expansion is reversible and adiabatic, then the entropy at 1 is known. If the pressure at 1 is measured the state at 1 and all its properties as well as the velocity there can be found by some method of extrapolation. (For example, it may be assumed that $p_1 v_1^k = p_0 v_0^k$ and the value of h_1 can thereupon be found from $h_1 = h_0 + \int_0^1 v dp$.) Equations [253], [254], and [255] then become expressions of the relation between the four unknowns, V_2 , v_2 , h_2 , and p_2 .

If we assume for the moment that the particles of fog at 2 are infinitely large (say, greater than 10^{-5} inch in diameter), the ordinary table of the properties of saturated liquid and saturated vapor yields a fourth relation between three of the four unknowns, namely, p_2 , h_2 , and v_2 , and offers the possibility of a unique solution for the state at 2. For one of Yellott's earlier tests* it is found that with a pressure at 1 of 13.7 lb/sq in. abs the computed pressure at 2 is 17.5 lb/sq in. abs. That is, according to the analysis, the course of the pressure is discontinuous at the point of condensation. The measured curve of pressures 0-1-3-4, Fig. 207, shows that such a discontinuity does exist although it is of lesser magnitude than the calculated one and is rounded off by the finite size of the hole through which the pressure is sampled. The curve 4-3 can be extrapolated back to the point of condensation 2', and a rough measure of the discontinuity in pressure ($p_2' - p_1$) can be had. For the test in question it was found to be 1.75 lb/sq in. instead of the computed value of 3.8 lb/sq in.

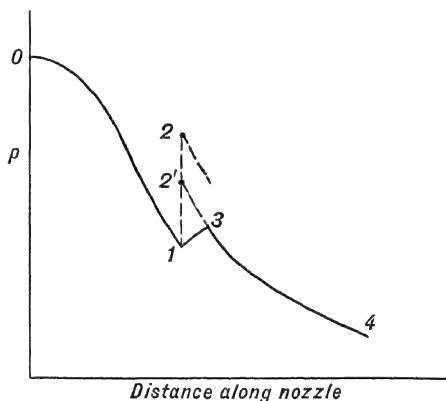


FIG. 207. Discontinuity in Pressure at the Point of Condensation

Behavior of a Stream if Small Drops Are Formed

A similar analysis can be made assuming that the fluid at 2 is an equilibrium mixture of vapor and drops of less than infinite radius. The equations [253], [254], and [255] still apply, but the ordinary tables of the properties of saturated liquid and saturated vapor do not. A table of properties of equilibrium mixtures of supersaturated vapor and any one

* *Trans. A.S.M.E.*, Vol. 56, pp. 427-430.

size of drop can be prepared from the Kelvin-Helmholtz relation and the properties of vapor and drops. Thus the natural log of the pressure of the vapor in equilibrium with a drop of radius r at a temperature T is given by

$$\ln p'' = \ln p_s + \frac{2\sigma v''}{rp_s v_g}, \quad [256]$$

where p_s and v_g refer to the normal saturation state at T . By extrapolation of the properties of the vapor phase the properties of the vapor corresponding to p'' and T can be found.

The specific volume of the liquid v' in [249] is the mean specific volume between the normal saturation pressure p_s and the pressure p' within the drop at the temperature in question. The two values can be found from a table of properties of the liquid by entering at the saturation conditions and again at the pressure

$$p' = p'' + \frac{2\sigma}{r}$$

according to [252]. (It is probable that extrapolation will be necessary from any existing table of the properties of compressed liquid, such as Table 4 of Keenan and Keyes, but the precision attained will be adequate.)

The energy of a drop of liquid is the sum of the energy of the material in the liquid phase and the energy of the film. If we assume the mass of the film to be negligible compared with the mass enclosed by it, we may write

$$u = u' + \frac{E}{F} \cdot \frac{F}{m'},$$

where u denotes the energy of unit mass of drops, u' the energy at p' and T of unit mass of liquid phase, E the surface energy of the film on one drop, F the surface area of the film, and m' the mass of the drop. Now

$$\frac{F}{m'} = \frac{Fv'}{\text{Vol}} = \frac{3v'}{r}$$

where Vol denotes the volume of the drop, v' its specific volume, and r its radius. Substituting this expression for F/m' and employing for E/F the expression [334] which is derived in Chapter XXVI, we get

$$u = u' + \frac{3v'}{r} \left[\sigma - T \left(\frac{\partial \sigma}{\partial T} \right)_{(p'-p'')} \right]. \quad [257]$$

Over a considerable range at low temperatures the experimental values of σ for flat surfaces can be represented by a linear equation:

$$\sigma = a + bT.$$

In view of the small effect on the energy of the stream of an error in the value of surface tension we may neglect the effect of curvature on σ . Then

$$-T \left(\frac{\partial \sigma}{\partial T} \right)_{(p', -p'')} = a,$$

and

$$u = u' + 3v'a \quad [258]$$

Now the relationship between the properties u , v , and p of an equilibrium mixture of vapor and drops of radius r in any proportion at temperature T can be found from [258] and the relations

$$u_m = \frac{m'u + m''u''}{m' + m''}$$

and

$$v_m = \frac{m'v' + m''v''}{m' + m''}$$

where subscript m refers to the mixture, superscript $'$ to the liquid and $''$ to the vapor, and u denotes the internal energy of unit mass of drops. The enthalpy of the mixture is

$$h_m = u_m + p''v_m,$$

where p'' is the pressure of the vapor.*

* The h - v - p relation for equilibrium mixtures of vapor and drops of various size can be represented satisfactorily for small proportions of drops by an equation of the type

$$h = mpv - n \log p + b.$$

Values of the coefficients of this equation, when h is in Btu/lb, p in lb/sq in. abs, and v in ft³/lb, are given below for drops of various radii, r .

$r \times 10^9$	m	n	b
ft			
∞	2.459	88.58	284.5
8	2.42	91.4	318.6
5	2.37	85.9	340.9
4	2.217	79.06	394.2
3	2.206	77.5	409.3

The state 2 in the nozzle may now be found for drops of various size, and the corresponding jump in pressure between 1 and 2 can be computed. The computed variation of the jump with size of drop for one set of test conditions is shown in Fig. 208. If the drops formed are

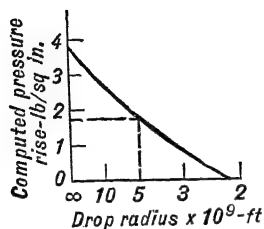


FIG. 208. Pressure Rise at Condensation as a Function of Drop Size

From *Trans. A.S.M.E.*, Vol. 56, pp. 427-430.

2.2×10^{-9} foot in radius no discontinuity will occur because this is the size of nuclei that are already present and any further increase in the number of nuclei will be a gradual and essentially continuous process. For the formation of larger drops the jump in pressure increases in magnitude until it reaches a maximum of 3.8 lb/sq in. for the formation of infinitely large drops. The jump deduced from the measurements indicates the formation of drops at section 2 with a radius of 5×10^{-9} foot, which grow suddenly from nuclei, with a radius of 2.2×10^{-9} foot. Figure 209 shows the agreement between the calculated jump in pressure and the measured jump for a number of tests plotted against the pressure before the nozzle. The calculations were all made for the formation of drops with a radius of 5×10^{-9} foot. The agreement appears to be good enough to justify the analysis.

The kinetic energy of the fluid stream immediately after the formation of the fine fog is less than it would have been if reversible expansion had occurred with the formation of large drops of liquid in equilibrium with the vapor. The amount by which it is less can be computed if the pressure after the point of condensation and the size of the drops that are formed are known. Since

$$\frac{V^2}{2g} = h_0 - h, \quad [253]$$

it is necessary only to know the enthalpy of the mixture immediately after condensation, which is one of the quantities determined in the preceding analysis, in order to find the kinetic energy of the stream at that point. The kinetic energy for isentropic expansion in equilibrium with large drops can be found directly from the *Steam Tables*.

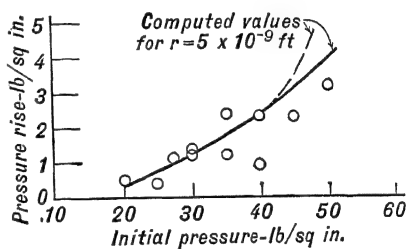


FIG. 209. Pressure Rise at Condensation

The circles represent experimental values. From *Trans. A.S.M.E.*, Vol. 56, pp. 427-430.

A similar calculation for loss of kinetic energy can be made for the pressure immediately before condensation. Here the loss is attributable to the failure of the steam to condense. The excess of the proportionate loss after condensation over that before condensation is due to the irreversibility of the process of condensation, which is in the nature of a shock.

Very little is known about the behavior of the mixture of vapor and drops as expansion proceeds beyond the point of condensation. During this process the temperature of the vapor will fall with falling pressure, but the temperature of the liquid will be reduced mainly by transfer of heat to the vapor. Temperature equilibrium will not be attained, because the drops will always be hotter than the vapor.

Under such conditions thermodynamics alone is of little use. It tells us the direction in which equilibrium lies and therefore the direction in which a change of state will proceed. It tells nothing, however, about the rate at which it will proceed. Since the solution of the problem of flow of a non-equilibrium mixture through a nozzle depends largely on the time rate at which transfers of mass and of heat occur, it must be sought through the principles of statistical mechanics or through empirical devices.

PROBLEMS

The surface tension of liquid water in dynes per centimeter in the presence of its own vapor is given to good precision by the equation

$$\sigma = 75.64 - 0.1391t - 0.0003t^2,$$

where t denotes the temperature in degrees Centigrade.

1. Find the diameter of the smallest drop of liquid that would grow in super-saturated vapor at 150 F and at a pressure twice the normal saturation pressure.
2. Derive an expression for the equilibrium pressure of a liquid surrounding a spherical bubble of vapor in terms of the normal saturation pressure p_s , the surface tension σ , and the radius of the bubble r . Assume that the density of the vapor is negligible as compared with that of the liquid.
3. Find the diameter of the smallest bubble that would grow in liquid at a temperature of 150 F and at an absolute pressure of zero.
4. How would you modify the Kelvin-Helmholtz relation for temperatures near the critical temperature, where the density of the vapor is not negligible compared with the density of the liquid and pv is not constant for constant temperature?
5. (a) Find the pressure immediately before the point of condensation for a reversible adiabatic expansion in a nozzle from the saturated condition at 20 lb/sq in. abs where the velocity is negligible. Assume that condensation begins when the

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enthalpy is 60 Btu/lb less than the initial value. Use any reasonable method of extrapolating the properties of the vapor phase.

(b) Find the size of the nuclei of condensation.

For (c) and (d) note the relations given in the footnote on page 445.

(c) Find the pressure immediately after the point of condensation if drops of infinite radius are formed.

(d) Find the same quantity if drops of radius 5×10^{-9} ft are formed.

SYMBOLS

E	surface energy of film on one drop
F	area of film surface
g	acceleration given to unit mass by unit force
h	enthalpy per unit mass
m	mass of film
p	pressure
p_*	pressure of vapor on flat surface
p''	pressure of vapor on curved surface
r	radius of curvature of surface
R	gas constant
T	absolute temperature
u	energy of unit mass
v	specific volume
V	velocity of fluid
Vol	volume of drop
W	work
y	vertical distance

GREEK LETTER

σ	surface tension
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SUBSCRIPTS

g	saturated vapor, normal saturation state
m	mixture
s	normal saturation state

SUPERSCRIPTS

'	liquid phase, drop
''	vapor phase

CHAPTER XXVI

CHEMICAL EQUILIBRIUM AND THE CHEMICAL POTENTIAL

A Generalized Expression for the Change in Energy

A system which is non-homogeneous in composition and in state may be considered to be made up of a number of smaller systems, subsystems, each of which is no smaller than is necessary to insure (at least to the first order of small quantities) homogeneity of composition and state. Such a subsystem we shall call a *phase*. For each phase we may write for a change of state

$$dE = T dS - p dV, \quad [259]$$

provided that the phase comprises always the same material and provided also that all the states between which the changes occur can be attained reversibly under no control other than a piston and a device for controlling temperature. For, in general, we may write

$$dE = T dS - dW \quad [260]$$

for any reversible process, where dW is the work done by the system. This equation is evidently equivalent to [259] if there is a reversible path between the states in question for which $dW = p dV$, that is to say, in the absence of gravity, capillarity, electricity, magnetism, distortion of solids, and relative motion of parts.

In the field of chemistry [259] can be generalized to include cases in which the state of the phase is altered by virtue of a transfer to it of the mass δm_1 of some substance 1 from some other part of the system. For example, gaseous oxygen might leave one part of a system to react chemically with carbon in another part, or to pass into solution in an aqueous part of the system, or to diffuse into a gaseous part. To allow for changes of state involving a transfer of mass into or out of a phase, we may expand [259] to

$$dE = T dS - p dV + \mu_1 dm_1 + \mu_2 dm_2 + \quad [261]$$

The new quantity μ_1 denotes the increase in energy of the phase per unit mass of substance 1 added to it while the entropy, the volume, and the masses of the other components 2, 3, etc., remain constant.

Interpretation of the Generalized Expression

Considered mathematically, μ_1, μ_2 , etc., are the differential coefficients of E taken with respect to the masses m_1, m_2 , etc. Under the restrictions imposed above, the state of a phase is fixed by two independent properties, such as S and V , provided that its composition is fixed. Therefore, the energy of the phase will be fixed by the quantities m_1, m_2 , etc., which determine composition and mass and by S and V . Thus

$$E = f(S, V, m_1, m_2, \dots),$$

where f denotes a function of the independent variables enclosed in parenthesis. Then, from the partial differential calculus, it follows that

$$dE = \frac{\partial E}{\partial S} dS + \frac{\partial E}{\partial V} dV + \frac{\partial E}{\partial m_1} dm_1 + \frac{\partial E}{\partial m_2} dm_2 + \quad [262]$$

where each partial derivative with respect to an independent variable is taken with all the other independent variables held constant.

This last expression must hold for any change of state, and therefore it must hold for one in which the entropy is altered while the volume and the composition remain unchanged. But under these conditions, by [259],

$$dE = T dS,$$

whereas, by [262],

$$dE = \frac{\partial E}{\partial S} dS.$$

It follows that

$$T = \left(\frac{\partial E}{\partial S} \right)_{V, m_1, m_2, \dots}$$

By similar reasoning we get

$$p = - \left(\frac{\partial E}{\partial V} \right)_{S, m_1, m_2, \dots}$$

Comparison of [261] with [262] will show that

$$\begin{aligned} \mu_1 &= \left(\frac{\partial E}{\partial m_1} \right)_{S, V, m_2, m_3, \dots} \\ \mu_2 &= \left(\frac{\partial E}{\partial m_2} \right)_{S, V, m_1, m_3, \dots} \quad \text{etc.} \end{aligned}$$

Selection of Component Substances

Usually the nature and number of the substances 1, 2, etc., is a matter of choice, and any chosen selection will be adequate provided that it fulfills the following conditions:

The selection must be sufficient in number to describe all possible transfers of mass across the boundary of the phase. For example, if the phase is exposed to possible transfer of hydrogen, oxygen, and water across its boundaries, then these three substances (or an equivalent three) must be included in the selection.

The selection must be restricted so that each dm is independent of every other. For example, if the phase is exposed to possible transfer of solutions of various concentrations of sulphuric acid in water, then anhydrous sulphuric acid and water are a sufficient selection to describe these transfers. It is not necessary to add to the selection solutions of various concentrations, because the magnitude of dm for one of these would not be independent of the magnitudes of dm for water and dm for anhydrous sulphuric acid.

The selection must include substances not present in the phase, provided that the phase is exposed to transfer of such substances. For example, a phase composed of anhydrous sulphuric acid which is surrounded by other phases containing water may change its state by absorbing water.

The Conditions of Equilibrium

It was shown on page 400 that "*for the equilibrium of any isolated system it is necessary and sufficient that in all possible variations in the state of the system which do not alter its entropy the variation of its energy shall either vanish or be positive.*"* If the symbol δ is used to indicate a variation in a property taken only to the first order relative to those which express the amount of change in the system, we may write the condition of equilibrium in the form

$$\delta E_s \geq 0. \quad [263]$$

If [263] is satisfied equilibrium may be of any kind — namely, stable, unstable, metastable, or neutral — but it cannot be what is sometimes called equilibrium due to passive resistance.

The condition [263] can be applied to a heterogeneous system in terms of the variations in energy of its homogeneous parts or phases. Thus, if we use accents to distinguish the properties of the various phases, [263] becomes

$$\delta E' + \delta E'' + \text{etc.} \geq 0$$

for all possible variations for which the entropy of the whole system does not change.

* Gibbs, *Collected Works*, Vol. 1, p. 56.

and that

$$\delta S' + \delta S'' + \text{etc.} = 0 \quad [b]$$

if the system is to be in equilibrium. If a variation of this sort is found for which the inequality holds in [a], then the reverse of this variation (in which the sign of each δS is reversed) would give

$$T' \delta S' + T'' \delta S'' + \text{etc.} < 0$$

and the system would not be in equilibrium. It follows that only the equality can hold; that is,

$$T' \delta S' + T'' \delta S'' + \text{etc.} = 0. \quad [c]$$

Since it is possible to have a variation involving one pair of phases and no others, it follows from the two equalities, [b] and [c], that

$$T' = T'' = \text{etc.} \quad [268]$$

That is, equilibrium will subsist only if the temperature of the system is uniform.

Similar considerations as regards infinitesimal possible variations for which the entropy and composition of each phase remain unchanged will show that it is necessary that

$$p' = p'' = \text{etc.} \quad [269]$$

That is, equilibrium will subsist only if the pressure of the system is uniform.

Equilibrium with Respect to Composition

Let us consider an infinitesimal possible variation for which the volume, the entropy, and the masses of all substances except substance 1 in each phase remain unchanged. Then the possible variation may consist of an increase δm_1 in the mass of substance 1 in any phase; and it may consist of a decrease in the mass of substance 1 in any phase in which substance 1 is an *actual* component. If in any phase substance 1 is a *possible* but not an *actual* component, then a possible variation may involve an increase in the mass of substance 1 in that phase, but not a decrease.

For possible variations of this sort it is necessary that

$$\mu'_1 \delta m'_1 + \mu''_1 \delta m''_1 + \text{etc.} \geq 0 \quad [270]$$

and

$$\delta m'_1 + \delta m''_1 + \text{etc.} = 0 \quad [271]$$

if the system is to be in equilibrium. Any pair of phases in which substance 1 is an actual component may exchange that substance in either direction. For such variations only the equality in the former expres-

sion can hold; and it follows that

$$\mu_1' = \mu_1'' \quad \text{etc.} \quad [272]$$

A phase in which substance 1 is a possible but not an actual component may receive that substance from any phase in which it is an actual component, but the reverse variation cannot occur. For example, if we refer to a phase that does not contain substance 1 by superscript x , and to one that does by superscript $'$, we may write for this variation, from [271],

$$\delta m_1^x = D \quad \text{and} \quad \delta m_1' = -D,$$

where D can denote only a positive number. The other condition [270] is that

$$D(\mu_1^x - \mu_1') \geq 0.$$

It follows that

$$\mu_1^x \geq \mu_1'. \quad [273]$$

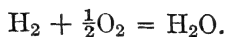
The quantity μ_1 is called the *chemical potential* of substance 1. Using this term we may sum up the conditions [264], [265], [266], and [267] which are necessary and sufficient for equilibrium of a heterogeneous system as follows: *The temperature and pressure must each be uniform throughout the system and the chemical potential for each of the component substances must have a constant value in all parts of the system of which that substance is an actual component, and have a value not less than this in all parts of which it is a possible component.**

The Equation of Chemical Equilibrium

In the preceding discussion of equilibrium the point was stressed that the component substances 1, 2, etc., must be so selected that all transfers of mass could be expressed in terms of masses δm_1 , δm_2 , etc., of these substances, and that these quantities δm_1 , δm_2 , etc., must be independent of each other. Now if there are three phases containing respectively water, a salt, and an aqueous solution of the salt, variations may be expressed in terms of masses of the substances salt and water, and these masses are independent of each other. On the other hand, if there are three phases containing respectively hydrogen, oxygen, and water, and the phase which contains one of these cannot contain either of the others, then for any variation the masses δm of any pair of the substances hydrogen, oxygen, and water are not independent of each other. When one mole of hydrogen leaves its phase to enter the water phase, one-half mole of oxygen will leave its phase, and one mole of water will enter its

* See J. W. Gibbs, *Collected Works*, Vol. 1, p. 67.

phase in accordance with the chemical equation



Thus, the chemical equation introduces a restriction into the conditions of equilibrium.

Suppose that among the components 1, 2, etc., which are comprised in an isolated system are the substances a , b , etc., which can combine (or dissociate) chemically to form substances k , l , etc. according to the relation

$$\alpha a + \beta b + \text{etc.} = \kappa k + \lambda l + \text{etc.} \quad [274]$$

This relation represents the usual equation of a chemical reaction. Symbols a , b , \dots k , l , \dots denote units of the corresponding substances, and α , β , \dots κ , λ , \dots denote numbers. Let us assume that each of these components is an actual component of some part of the system.

If the system is in equilibrium then the conditions [273] must hold, and in all phases in which the substance a appears (as a separately variable compound — not in chemical combination) the value of μ_a must be the same. We shall denote this common value by M_a . For phases which do not contain substance a the value of μ_a cannot be less than M_a , so that in general

$$\mu_a \geq M_a. \quad [275]$$

Similar statements may be made concerning μ_b , μ_k , etc.

The conditions of equilibrium require that, for any variation at constant entropy,

$$\begin{aligned} \delta E &= T' \delta S' - p' \delta V' + \mu'_a \delta m'_a + \mu'_b \delta m'_b + \dots \mu'_k \delta m'_k + \dots \\ &+ T'' \delta S'' - p'' \delta V'' + \mu''_a \delta m''_a + \mu''_b \delta m''_b + \dots \mu''_k \delta m''_k + \dots \\ &+ \text{etc.} \\ &\geq 0. \end{aligned} \quad [276]$$

Now let us consider a possible variation for which

$$\delta S' = 0 = \delta S'' = \text{etc.},$$

$$\delta V' = 0 = \delta V'' = \text{etc.},$$

and for which the masses δm_a , δm_b , etc., of substances a , b , etc., leave phases in which they are actual components to unite chemically and form masses δm_k , δm_l , etc., of substances k , l , etc., in phases in which these are actual components. Let δm denote a certain small number of units of the kind employed in [274]. Then we may denote the gain in mass of substance k in a phase in which it is an actual component by $\kappa \delta m$, and, by [274], the gain in mass of substance l by $\lambda \delta m$, that of

substance a by $(-\alpha\delta m)$ (since a gain in k , l , etc., must be compensated by a loss in a , b , etc.), that of substance b by $(-\beta\delta m)$, etc.

Since substance a is an actual component of the phase which it enters or leaves, we have for any such phase

$$\mu_a = M_a,$$

and similarly as regards the other substances. Now we may write [276] for the variation in question

$$\begin{aligned}\delta E &= -\alpha M_a \delta m - \beta M_b \delta m \cdots + \kappa M_k \delta m + \lambda M_l \delta m + \cdots \\ &= -(\alpha M_a + \beta M_b \cdots - \kappa M_k - \lambda M_l \cdots) \delta m \\ &\geq 0.\end{aligned}$$

The quantity δm may be positive or negative, depending on the assumed direction of the reaction; therefore, only the equality can hold, and we get

$$\alpha M_a + \beta M_b + \cdots = \kappa M_k + \lambda M_l + \cdots. \quad [277]$$

This is the *equation of chemical equilibrium*. Unless it is satisfied equilibrium cannot subsist in an isolated system.

The equation of chemical equilibrium can be obtained from the equation of the chemical reaction [274] by substituting the chemical potentials, M_a , M_b , etc., for the units, a , b , etc. It is easy to see that, if there are a number of equations [274] relating to a number of possible chemical reactions between components of the system, there will be a corresponding number of equations of equilibrium similar to [277].

The Chemical Potential of a Pure Substance

If we apply [261] to a phase of a pure substance we have

$$dU = T dS - p dV + M dm, \quad [278]$$

where U is substituted for E , and, since they are identical for an actual component, M is substituted for μ . The magnitude of M is fixed by the state of the fluid, which is in turn fixed by T and p . Therefore [278] may be integrated at constant pressure and temperature from a vanishingly small mass to a finite mass m . The result is

$$U = TS - pV + mM,$$

from which we get

$$M = \frac{U + pV - TS}{m}.$$

or

$$M = \zeta. \quad [279]$$

Thus, the chemical potential of a pure substance is identified as the value of Z per unit mass.

Equilibrium of a Heterogeneous System with a Pure Substance

Consider a heterogeneous system comprising n substances among which is the substance 1. Let the system be enclosed by an envelope, one part of which is a membrane which separates the system from a mass of pure substance 1 (Fig. 210). This membrane permits the substance 1 to pass through it in either direction, but it prevents the passage of other substances, including chemical compounds of which substance 1 is a part. If there is any resistance to the passage of substance 1 through the membrane we shall assume it to be of the nature of a viscous resistance; that is, it vanishes with the velocity of the current.

Any membrane which fulfills these requirements is known as a *semipermeable membrane*. Perfect semipermeable membranes do not occur in nature, but various approximations to perfection are found. For example, palladium is permeable to hydrogen at high temperatures while it is essentially impermeable to nitrogen and other gases. The perfect semipermeable membrane, like the reversible process, is an analytical tool of great utility regardless of the impossibility of realizing it in practice.

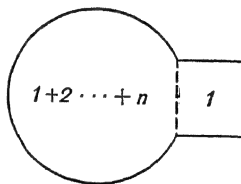


FIG. 210

For equilibrium of this system the conditions [264] to [267] must be satisfied as in the more general case. We can show, therefore, by means of suitable possible variations that the temperature of all phases, including the pure phase consisting of substance 1, must be the same, and that μ_1 must be the same in all phases of which substance 1 is an actual component, including the pure phase. Thus, we get for the chemical potential of substance 1 in all phases of which it is an actual component

$$\mu_1 = M_1 = \zeta_1, \quad [280]$$

where ζ_1 is the property ($u + pv - Ts$) of the pure phase. If we include phases in which substance 1 is a possible but not an actual component, we have

$$\mu_1 \geq M_1 = \zeta_1.$$

By possible variations in the volumes of the phases we can show, as was done above, that the pressures of all phases whose volumes are not fixed by intervening membranes must be the same. Let us consider, however, the pure phase on one side of the semipermeable membrane and the "mixture phase," which includes substance 1, on the other side. There are possible variations in the volume of the pure phase toward larger or smaller volumes, since the membrane does not prevent its

passage. On the other hand, there is no possible variation in the volume of the mixture phase through the membrane toward larger volume, though there are possible variations toward smaller volume. Therefore, it can be shown that the pressure in the mixture phase cannot be less than the pressure in the pure phase. In general it will be greater.

Equilibrium of Pure Phases of Substances that Can React Chemically

Consider a heterogeneous system comprising the component substances $a, b, \dots k, l, \dots$. Let us assume that some of these substances can react chemically according to the chemical equation

$$\alpha a + \beta b + \dots = \kappa k + \lambda l + \dots,$$

and that each of these substances in a pure phase is in equilibrium with the heterogeneous system through an appropriate semipermeable membrane (Fig. 211).

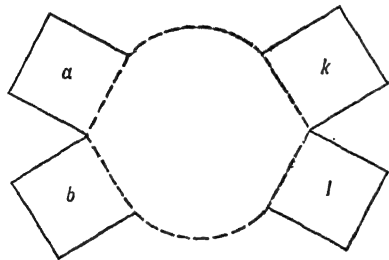


FIG. 211

Now a possible variation consists of a transfer of masses $\alpha\delta m, \beta\delta m$, etc., from the pure phases a, b , etc., into the composite phases, where reaction occurs to form masses $\kappa\delta m, \lambda\delta m$, etc., of components k, l , etc. If we add to this variation one for which the masses $\kappa\delta m, \lambda\delta m$, etc., of k, l , etc., leave the composite phases and enter the pure phases k, l , etc.,

then the entire variation will consist of a transfer of mass from the pure phases a, b , etc., to the pure phases k, l , etc., without effect on the composite phases. Such a variation at constant entropy and volume of each phase results in an equation of equilibrium in the form

$$\alpha\zeta_a + \beta\zeta_b + \dots = \kappa\zeta_k + \lambda\zeta_l + \quad [281]$$

where each ζ is a property of a pure phase in equilibrium with the composite phase. This is a condition for equilibrium of the composite phase whether or not substances are present other than those appearing in the chemical equation.

The Equilibrium Constant in Terms of Partial Pressures

The equation of equilibrium can be further simplified if each of the pure substances behind its semipermeable membrane can be considered a perfect gas. Since the enthalpy of a perfect gas is a function of temperature only, and its specific heat at constant pressure is constant (Chapter IX), the enthalpy and the entropy of a unit mass may be stated

in the forms

$$h = h' + c_p T, \quad [282]$$

and

$$s = s' + c_p \ln T - R \ln p, \quad [283]$$

where h' , c_p , s' , and R are constants for any one gas. Upon combining these with the definition of ζ we get

$$\begin{aligned} \zeta &= h - Ts \\ &= RT \ln p + y, \end{aligned} \quad [284]$$

where y is a function of temperature only. If we substitute this expression into the equation of equilibrium [281], and then transpose and divide by T , we get

$$\alpha R_a \ln p_a + \beta R_b \ln p_b + \cdots - \kappa R_k \ln p_k - \lambda R_l \ln p_l - \cdots = Y, \quad [285]$$

where Y is a function of temperature only for any one reaction. Each R is the universal gas constant if the molecular weight of each substance is chosen as its unit of mass, or

$$R_a = R_b = \cdots = R.*$$

Substituting in [285] and dividing through by R , we get

$$\alpha \ln p_a + \beta \ln p_b + \cdots - \kappa \ln p_k - \lambda \ln p_l - \cdots = Y',$$

where Y' is Y/R . Taking the antilog we find that

$$\frac{p_k^{\kappa} p_l^{\lambda} \cdots}{p_a^{\alpha} p_b^{\beta} \cdots} = K_p, \quad [286]$$

where K_p is a function of temperature only and is therefore a constant for any one temperature. It is called the *equilibrium constant* in terms of partial pressures. It should be noted that the exponent of each pressure is the coefficient of the corresponding substance in the chemical equation [274].

Values of the equilibrium constant in terms of pressure for a number of chemical reactions are shown in Fig. 212 as functions of temperature.

* If one prefers to use the same unit of mass for all substances, then one gets

$$R_a = \frac{R}{m_a}, \quad R_b = \frac{R}{m_b}, \text{ etc.,}$$

where m_a , m_b , etc., are the molecular weights of the substances a , b , etc. Then in everything that follows α/m_a will appear in place of α , etc.

The value of K_p is that computed from [286] using pressures in atmospheres.

It is desirable to relate the equilibrium constant to the pressure of the mixture enclosed by the semipermeable membranes. For this purpose we shall use Gibbs's statement of an empirical principle which often holds true at low pressures to a high degree of approximation. It is

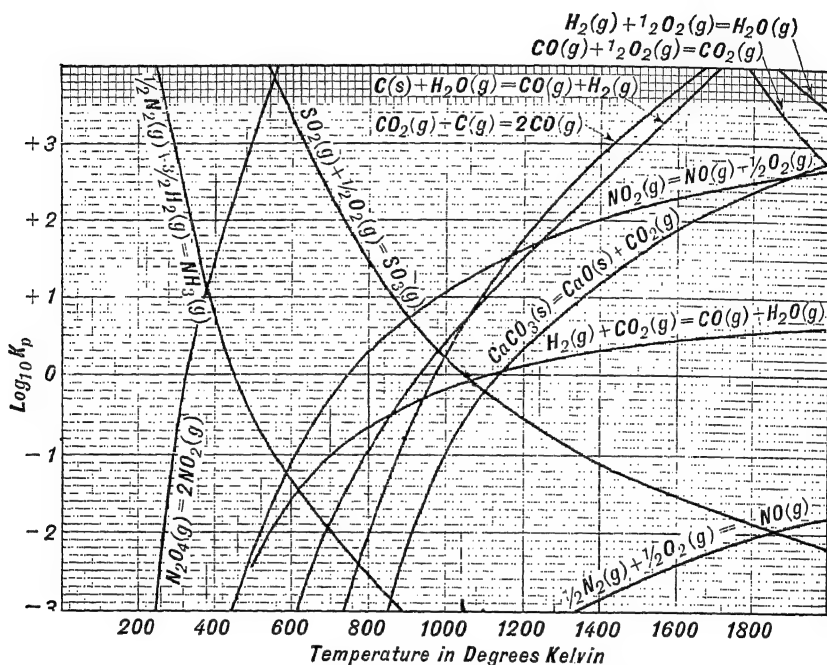


FIG. 212. Equilibrium Constants of Chemical Reactions

Reacting concentrations are expressed in terms of partial pressures in atmospheres. From Hougen and Watson, *Industrial Chemical Calculations*, Wiley, 1931, p. 474.

known as the Gibbs-Dalton Law: *The pressure in a mixture of different gases is equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and with the same value of its (chemical) potential.* Since the chemical potential of a component gas is the same on either side of the membrane which is permeable to it, we may write

$$p = p_a + p_b \cdots + p_k + p_l \cdots \quad [287]$$

This equation and the equation of chemical equilibrium constitute two simultaneous equations in terms of the pressures of the pure substances.

The Equilibrium Constant in Terms of Concentrations

We shall follow Gibbs's method of showing that the Gibbs-Dalton Law demands that the concentration (the mass per unit volume) of each substance in the mixture should be the same as its density in the pure phase in equilibrium with the mixture.

It was shown above that, for any phase of a system that is homogeneous in state, we may write

$$dE = T dS - p dV + \mu_1 dm_1 + \mu_2 dm_2 + \cdots \quad [261]$$

for any change within the limitations prescribed on page 449, between states of equilibrium. If this equation is integrated at constant pressure and temperature from a mass of zero to any finite mass at constant composition — that is, if the values of dE for each element of the homogeneous mass are summed up — we get for the internal energy of the phase the expression

$$E = TS - pV + \mu_1 m_1 + \mu_2 m_2 + \cdots, \quad [288]$$

which when differentiated in the most general way gives

$$\begin{aligned} dE = T dS + S dT - p dV - V dp + \mu_1 dm_1 + m_1 d\mu_1 \\ + \mu_2 dm_2 + m_2 d\mu_2 + \cdots. \end{aligned} \quad [289]$$

Subtracting [261] from [289] we get

$$S dT - V dp + m_1 d\mu_1 + m_2 d\mu_2 + \cdots = 0. \quad [290]$$

Since this expression, like [261], holds true for any change between states of equilibrium it may be applied to a mixture of gases in equilibrium through semipermeable membranes with pure phases of the constituents of the mixture. It may also be

applied to any one of the pure phases. Let us apply it first to the mixture while a piston which confines the pure phase of substance 1 is pushed inward. At the same time the temperature of all parts and the pressures of the other pure phases

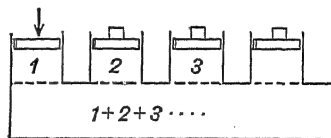


FIG. 213

are to be held constant (Fig. 213). Since the pressure and temperature of each of the pure phases, except phase 1, remain unaltered, the state of each and therefore the chemical potential (which is equivalent to the value of ζ) also remain unaltered. But, for equilibrium, the chemical potential of each substance must be the same on either side of its semipermeable membrane. Therefore, the chemical potential of each constituent of the mixture, except substance 1, remains unchanged. For

the mixture in this case [290] takes the form

$$-V dp + m_1 d\mu_1 = 0. \quad [291]$$

For the pure phase 1 it is

$$-V_1 dp_1 + m'_1 d\mu'_1 = 0, \quad [292]$$

where each symbol refers to a property of the pure phase. But for equilibrium the chemical potential of substance 1 must remain the same on both sides of the membrane, and therefore

$$d\mu_1 = d\mu'_1.$$

Also, by the statement of the Gibbs-Dalton Law given above, the pressure of the mixture must increase by the same amount as the pressure of the pure phase, for the pressures of the other pure phases remain unaltered; that is,

$$dp = dp_1.$$

Substituting these equalities in [291] and [292] we get

$$\frac{V_1}{m'_1} \frac{d\mu_1}{dp} = \frac{V}{m_1}, \quad [293]$$

or the concentration of substance 1 in the mixture is the same as its density in the pure phase with which the mixture is in equilibrium. If the concentration of the substance 1 in the mixture is denoted by c_1 , we may write

$$c_1 = \frac{1}{v_1}, \quad [294]$$

where v_1 is the specific volume of the pure phase. It also follows that the density of the mixture is the sum of the densities of the pure phases with which it is in equilibrium: thus

$$\begin{aligned} \frac{m}{V} &= \frac{m_1}{V} + \frac{m_2}{V} + \dots \\ &= \frac{m'_1}{V_1} + \frac{m'_2}{V_2} + \dots \\ &= \frac{1}{v_1} + \frac{1}{v_2} + \dots \end{aligned} \quad [295]$$

For the pressure of the pure phase of each perfect gas we may write an equation of the sort

$$p_1 = \frac{RT}{v_1},$$

if v_1 denotes the volume of the phase per mole. Then, by [294],

$$p_1 = RTc_1, \quad [296]$$

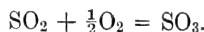
where R denotes the universal gas constant and c_1 the molal concentration of substance 1, that is, the number of moles of substance 1 per unit volume of the mixture. Substituting [296] in [286] we get

$$\frac{c_k^\kappa c_l^\lambda}{c_a^\alpha c_b^\beta \dots} = K_c, \quad [297]$$

where K_c is the equilibrium constant in terms of concentrations. Like K_p it is a function of temperature only, and it is related to K_p in the following way

$$K_c = K_p (RT)^{\alpha+\beta+\dots-\kappa-\lambda-\dots}.$$

EXAMPLE. To illustrate the use of the equilibrium constant we shall calculate the degree of dissociation of sulphur trioxide into sulphur dioxide and oxygen in accordance with the chemical equation



In terms of the symbols used above, we may write this

$$a + \frac{1}{2}b = k.$$

From Fig. 212 we find the equilibrium constant in terms of pressure at a temperature of 1050 K to be

$$K_p = \frac{p_k}{p_a p_b^{1/2}} = 1 \text{ atm}^{-1/2}.$$

The corresponding value of the equilibrium constant in terms of concentration is

$$K_c = \frac{c_k}{c_a c_b^{1/2}} = K_p (RT)^{1/2} = 1 \times \sqrt{82.06 \times 1050} = 294 \text{ (cm}^3/\text{mole)}^{1/2}.$$

Now let us assume that all SO_2 and all O_2 present in the state of equilibrium are products of the dissociation of SO_3 . It follows from the chemical equation that there will be one mole of SO_2 and one-half mole of O_2 for each mole of SO_3 that dissociates. Let ϵ denote the fraction of SO_3 dissociated. Then the equilibrium concentration of SO_3 can be expressed as

$$c_k = (1 - \epsilon)c_0,$$

where c_0 represents the concentration of SO_3 when ϵ is zero. The concentrations of the other substances are then

$$c_a = \epsilon c_0, \quad \text{and} \quad c_b = \frac{1}{2}\epsilon c_0.$$

The constants of equilibrium are now given by

$$\frac{\sqrt{2}(1 - \epsilon)}{c_0} c_0^{-1/2} = K_c = K_p (RT)^{1/2}. \quad [298]$$

The pressure of the equilibrium mixture may be expressed as the sum of the partial pressures, and these in turn may be expressed in terms of the fraction of SO_3 dissociated:

$$\begin{aligned} p &= p_a + p_b + p_k = RT(c_k + c_a + c_b) \\ &= RTc_0(1 - \epsilon + \epsilon + \tfrac{1}{2}\epsilon) = RTc_0(1 + \tfrac{1}{2}\epsilon). \end{aligned}$$

Thus, we get for c_0

$$c_0 = \frac{p}{RT} (1 + \tfrac{1}{2}\epsilon)^{-1}.$$

Substituting back into [298] and rearranging, we get

$$\sqrt{2}(1 - \epsilon)(1 + \tfrac{1}{2}\epsilon)^{1/2} = K_p p^{1/2},$$

or

$$p = \frac{2}{K_p^2} \frac{(1 - \epsilon)^2(1 + \tfrac{1}{2}\epsilon)}{\epsilon^3}. \quad [299]$$

This relation between the fraction dissociated and the pressure is shown in Fig. 214. Dissociation will be complete at zero pressure for any temperature

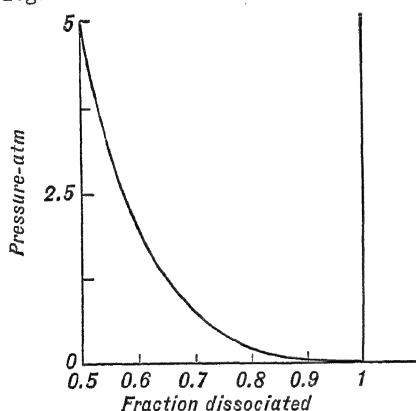


Fig. 214. Dissociation of SO_3 at 1050 K

for which K_p is finite. At a pressure of 1 atmosphere the sulphur trioxide is 73 per cent dissociated; at 10 atmospheres it is half dissociated.

The value of K_p for this reaction increases with decrease in temperature (Fig. 212). It can be seen from [299] that the pressure corresponding to a given degree of dissociation will decrease with decrease in temperature. The ordinates of the curve of Fig. 214 would be reduced to 1 per cent of the values shown if the temperature were reduced from 1050 K to 860

K. Thus the stability of SO_3 increases with decrease in temperature or with increase in pressure.

The Equilibrium Constant in Terms of Mole Fractions

The mole fraction of substance 1 in the mixture is defined as

$$x_1 = \frac{c_1}{c_1 + c_2 + \dots}$$

or

$$x_1 = \frac{c_1}{\rho},$$

where ρ is the density of the mixture in moles per unit volume. But for each pure phase we may write [296]

$$p_1 = \frac{RT}{v_1} = RTc_1,$$

and for all the pure phases we get the summation

$$\sum p_1 = RT \sum c_1 = RT\rho.$$

Then by the Gibbs-Dalton Law we get for the mixture

$$p = RT\rho.$$

Therefore, the mole fraction can be expressed as a ratio of pressures:

$$x_1 = \frac{c_1}{\rho} = \frac{p_1}{p}. \quad [300]$$

Expressing each pressure in [286] in terms of a mole fraction, we get for equilibrium

$$\frac{x_k^\alpha x_l^\lambda}{x_a^\alpha x_b^\beta \cdots} = K_p p^{\alpha+\beta \cdots -\kappa-\lambda \cdots} = K_x, \quad [301]$$

where K_x is called the equilibrium constant in terms of mole fractions. It should be noted that whereas Y , K_p , and K_c above are functions of temperature only, K_x is a function of pressure and temperature. Therefore, it is constant only for constant temperature and constant pressure of the mixture. However, it is independent of pressure if the number of moles of the products is identical with that of the reactants; that is, if

$$\alpha + \beta \cdots - \kappa - \lambda \cdots = 0.$$

The Fugacity

For perfect gases which obey the Gibbs-Dalton Law we find that the equation of equilibrium [277] can be reduced to the statement [286] that a certain product of powers of the partial pressures of the gases is a constant. By analogy we may deduce a property comparable to the pressure of a perfect gas in terms of which the equation of equilibrium can be similarly reduced for other substances. To do this we need only define a new property in such a way that M of [277] is a logarithmic function of the new property.

It was shown above that the value of the chemical potential for the pure phase of a perfect gas is

$$\zeta = RT \ln p + y, \quad [284]$$

where y is a function of temperature only. By analogy, let us define a quantity f as follows:

$$\zeta = RT \ln f + y, \quad [302]$$

where y is again a function of temperature only. This new quantity f , which is evidently a property, is called the *fugacity*.

We may substitute [302] in [281] to get a new equilibrium constant of the form

$$\frac{f_k^\kappa f_l^\lambda \cdots}{f_a^\alpha f_b^\beta \cdots} = \text{constant}. \quad [303]$$

This statement is not limited in its application, like [286], [297], and [301], to perfect gases or to substances which obey the Gibbs-Dalton Law. It is as general as the equation of chemical equilibrium.

The Escaping Tendency

Equilibrium may be thought of as a balance of active forces. When a system comprises several homogeneous parts with the same actual components, then for equilibrium the tendency for any one component to escape from one part must be the same as its tendency to escape from all other parts. For this condition it has been shown above that the chemical potential of the component is the same in all parts of the system.

If a component of a system in equilibrium is a possible but not an actual component of a part of the system, then the tendency of the component to escape from that part must be greater than (or, in the limit, equal to) its tendency to escape from the parts of which it is an actual component. For this condition it has been shown above that the chemical potential of the component is greater (or, in the limit, no different) in the part in which it is not present than in those parts which include it.

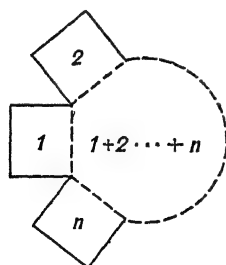


FIG. 215

Thus, by analogy, the chemical potential of a component of a system is often thought of as a measure of the *escaping tendency* of that component. The fugacity can be similarly interpreted.

Further Consequences of the Gibbs-Dalton Law

Consider a mixture of n substances, 1, 2, \cdots , n , which conforms to the Gibbs-Dalton Law. Let it be enclosed in an envelope consisting of n

semipermeable membranes each of which separates the mixture from a mass of one of the substances in the pure form (Fig. 215). The Gibbs-Dalton Law may be stated in the form

$$p_m = p_1 + p_2 \cdots + p_n, \quad [304]$$

where subscript m refers to the mixture and subscripts $1, 2, \cdots n$ refer to the pure phases. It was shown on page 453 that for equilibrium it is necessary that

$$t_m = t_1 = t_2 \cdots = t_n, \quad [305]$$

and

$$\mu_1 = \mu_{1m}, \quad \mu_2 = \mu_{2m}, \cdots \mu_n = \mu_{nm}, \quad [306]$$

where subscripts $1m, 2m, \cdots nm$ refer to the components in the mixture. Furthermore on page 462 it was shown that

$$\frac{1}{v_1} = c_{1m}, \quad \frac{1}{v_2} = c_{2m}, \quad \cdots = c_{nm}, \quad [307]$$

where each c denotes the concentration of a component in the mixture, and that, therefore,

$$\frac{1}{v} = \frac{1}{v_1} + \frac{1}{v_2} + \cdots + \frac{1}{v_n}. \quad [308]$$

Here we shall show how other properties of the mixture may be obtained from properties of the pure components in equilibrium with the mixture.

On page 461 two basic equations were developed for a heterogeneous system, namely,

$$E = TS - pV + \mu_1 m_1 + \mu_2 m_2 \cdots + \mu_n m_n \quad [288]$$

and

$$S dT - V dp + m_1 d\mu_1 + m_2 d\mu_2 \cdots + m_n d\mu_n = 0, \quad [290]$$

where $m_1, m_2, \cdots m_n$ denote the masses of the corresponding substances in a phase, and symbols without subscripts denote properties of the phase. These may be applied either to the mixture or to one of the pure phases in equilibrium with it. Let us apply [290] first to a process at constant $\mu_1, \mu_2, \cdots \mu_n$ in the mixture and at constant μ in each pure phase. We get, upon dividing through by dT ,

$$S_m = V_m \left(\frac{\partial p_m}{\partial T} \right)_{\mu_1, \mu_2, \dots, \mu_n}, \quad S_1 = V_1 \left(\frac{\partial p_1}{\partial T} \right)_{\mu_1}, \quad S_2 = V_2 \left(\frac{\partial p_2}{\partial T} \right)_{\mu_2}, \text{ etc.} \quad [309]$$

If we differentiate the statement [304] of the Gibbs-Dalton Law at

constant values of the chemical potentials, we get

$$\left(\frac{\partial p_m}{\partial T}\right)_{\mu_1, \mu_2, \dots, \mu_n} = \left(\frac{\partial p_1}{\partial T}\right)_{\mu_1} + \left(\frac{\partial p_2}{\partial T}\right)_{\mu_2} + \text{etc.}, \quad [310]$$

which may be substituted in [309]. Now let us apply [309] to a volume of the pure phase of component 1 which is equal to the volume of the mixture. We get for component 1

$$S_1 = V \left(\frac{\partial p_1}{\partial T}\right)_{\mu_1}, \quad [311]$$

and similar expressions for each of the other components. Combining [309], [310], and [311], we get

$$S_m = S_1 + S_2 \cdots + S_n.$$

Since the volumes for which S_m , S_1 , S_2 , etc., are the entropies are identical and since the mass of each component is the same for identical volumes of its pure phase and of the mixture, the equation for entropy becomes

$$m_m s_m = m_1 s_1 + m_2 s_2 \cdots + m_n s_n, \quad [312]$$

where m_1 , m_2 , etc., are the masses of components 1, 2, etc., in the mass m of mixture.

To find a similar relation between the energies we substitute in [288] the values for p and S given by [304] and [312] and rearrange: thus

$$E_m = (Tm_1 s_1 - p_1 V + \mu_1 m_1) + (Tm_2 s_2 - p_2 V + \mu_2 m_2) + \text{etc.},$$

where m_1 is the mass of component 1 in a volume V of the pure phase as well as in a volume V of the mixture. Therefore, we may write the last equation in the form

$$m_m u_m = m_1 (Ts_1 - pv_1 + \mu_1) + m_2 (Ts_2 - pv_2 + \mu_2) + \text{etc.}$$

But each parenthesis is by [288] the energy per unit mass of a pure phase. It follows that

$$m_m u_m = m_1 u_1 + m_2 u_2 \cdots + m_n u_n. \quad [313]$$

From the relations proved above it is easy to show that

$$m_m h_m = m_1 h_1 + m_2 h_2 \cdots + m_n h_n,$$

$$m_m \psi_m = m_1 \psi_1 + m_2 \psi_2 \cdots + m_n \psi_n,$$

and

$$m_m \xi_m = m_1 \xi_1 + m_2 \xi_2 \cdots + m_n \xi_n.$$

Azeotropic Mixtures

The boiling points of the pure components of a mixture do not always correspond to the maximum and minimum boiling points of the mixture as in Fig. 171. When the boiling temperature passes through a maximum or a minimum at an intermediate composition, as in Fig. 216, the composition of the vapor is identical with that of the liquid with which it is in equilibrium. That is, the condensation line and the boiling line coincide at the maximum or minimum. Such a mixture is called an *azeotrope* or an *azeotropic mixture*. When it is boiled its temperature

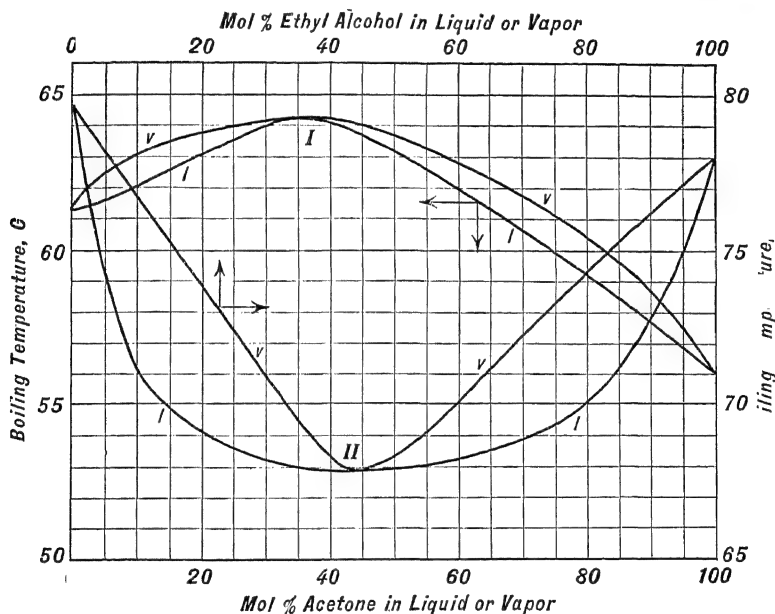


FIG. 216. Isobaric Boiling-Point Curves at 750 mm Hg

I Acetone-Chloroform. II Benzene-Ethyl Alcohol.

The curves labeled v mark the beginning of condensation in cooling and those labeled l mark the beginning of vaporization in heating. From Hougén and Watson, *Industrial Chemical Calculations*, Wiley, 1931, p. 433.

does not rise with time as does the temperature of ordinary mixtures. Therefore it is sometimes called a *constant-boiling mixture*.

To show that a constant-boiling mixture must be a mixture of maximum or minimum boiling point,* we shall first write $[290]$ for each of the phases, using a single accent to distinguish properties of the liquid

* This treatment is given by Butler in *Commentary on the Scientific Writings of J. W. Gibbs*, Yale University Press, 1936, pp. 111-112, following Gibbs's derivation on pp. 99-100 of Vol. 1 of the *Collected Works*.

phase and a double accent to distinguish those of the vapor phase: thus

$$V' dp = S' dT + m'_1 d\mu_1 + m'_2 d\mu_2$$

and

$$V'' dp = S'' dT + m''_1 d\mu_1 + m''_2 d\mu_2,$$

where for equilibrium p , T , μ_1 , and μ_2 must be respectively the same for both phases. Eliminating $d\mu_2$ from these equations we get

$$(V'm''_2 - V''m'_2)dp = (S'm''_2 - S''m'_2)dT + (m'_1m''_2 - m''_1m'_2)d\mu_1; \quad [314]$$

and from this it follows that at constant pressure

$$\frac{dT}{d\mu_1} = - \frac{m'_1m''_2 - m''_1m'_2}{S'm''_2 - S''m'_2},$$

and at constant temperature

$$\frac{dp}{d\mu_1} = \frac{m'_1m''_2 - m''_1m'_2}{V'm''_2 - V''m'_2}.$$

For a constant-boiling mixture we may write

$$\frac{m'_1}{m'_2} = \frac{m''_1}{m''_2},$$

$$m'_1m''_2 = m''_1m'_2, \quad [315]$$

which when substituted in the previous equations gives for constant pressure

$$\frac{dT}{d\mu_1} = 0,$$

and for constant temperature

$$\frac{dp}{d\mu_1} = 0.$$

Therefore, the temperature of a constant-boiling mixture is either a maximum or a minimum for a given pressure, and the pressure of such a mixture is either a maximum or a minimum for a given temperature.

Substituting the condition [315] for a constant-boiling mixture into [314] and dividing through by $m'_1m''_2$, we get

$$\left(\frac{V'}{m'_2} - \frac{V''}{m''_2}\right)dp = \left(\frac{S'}{m'_2} - \frac{S''}{m''_2}\right)dT,$$

which when multiplied through by the ratio of the mass of substance

2 in either phase to the total mass of the phase becomes

$$\left(\frac{V'}{m'} - \frac{V''}{m''}\right)dp = \left(\frac{S'}{m'} - \frac{S''}{m''}\right)dT,$$

or

$$\frac{dp}{dT} = \frac{s' - s''}{v' - v''}.$$

This is the Clapeyron equation which was shown in Chapter XIX to hold for a pure substance. Here it is shown to hold for an azeotropic mixture as well.

If a binary mixture is azeotropic in some proportions (Fig. 216) it cannot be completely rectified in the simple tower described in Chapter XXII. However, the azeotropic mixture, which is so like a pure substance in its constancy of composition during evaporation and in its conformity to the Clapeyron relation, may be treated as a constituent of the mixture and separated from one of the pure constituents by rectification. To separate the other pure constituent the pressure must be changed until the mixture in question is no longer azeotropic.

The Effect of Pressure on the Vapor Pressure of a Liquid

If a liquid is separated from a gas by a wall of porous material of sufficiently fine structure no liquid will pass through the wall without changing to the vapor phase. That is, the capillary action of the liquid in the pores will hold the liquid even against a substantial difference in pressure. The porous wall may be considered a semipermeable membrane which is permeable to the vapor phase but not to the liquid phase.

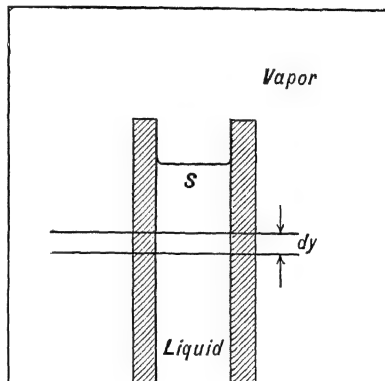


FIG. 217. Equilibrium of Vapor and Liquid through a Porous Wall

If we place within a chamber filled with the vapor of a pure substance a porous tube containing the same substance in the liquid phase, the pressure and temperature of the contents of the chamber may be adjusted until the vapor and the liquid surface (*S*, Fig. 217) are in equilibrium. For this condition it follows from [280] that the chemical potential of the substance in the two phases must be the same in the neighborhood of the liquid surface. Since the chemical potential of a substance in

any of its pure phases is by [279] identical with the value of ζ , then

$$\zeta' = \zeta'',$$

where ' denotes the liquid phase and '' denotes the vapor phase.

Under the influence of gravity the pressure of each phase will increase with depth. For an increase in depth dy the pressure of the liquid phase increases by dy/v' , or

$$\left. \begin{aligned} dy &= v' dp' \\ dy &= v'' dp'' \end{aligned} \right\} \quad \text{[316]}$$

But since, by definition,

$$\zeta = h - Ts$$

then

$$d\zeta = du + p dv + v dp - T ds - s dT.$$

However,

$$du + p dv = T ds,$$

so that

$$d\zeta = v dp - s dT.$$

Therefore, at constant temperature

$$d\zeta = v dp = dy,$$

and

$$d\zeta' = dy = d\zeta''. \quad \text{[317]}$$

It follows that if ζ' and ζ'' are identical at the level of the surface of the liquid they are identical at all levels below the surface. Therefore, the liquid and vapor are in equilibrium at all levels.

Let us determine the relation between the pressure of the liquid at any level and the pressure of the vapor in equilibrium with it. At any depth y below the surface of the liquid the pressure p' of the liquid is given by

$$y = \int_{p_s}^{p'} v' dp' = v'(p' - p_s),$$

where p_s denotes the pressure at the surface S , and the specific volume of the liquid is assumed to be constant. If the pressure of the vapor is low enough, we may assume that

$$pv = RT = p_s v_g,$$

where v_g denotes the specific volume of the vapor at S . Then we get

$$y = \int_{p_s}^{p''} v' dp'' = RT \ln \frac{p''}{p_s},$$

where p'' denotes the pressure of the vapor in equilibrium with the liquid at pressure p' . Combining the last two equations, we get

$$\ln \frac{p''}{p} = \frac{v'(p' - p)}{RT} \quad [318]$$

The quantity p'' may be called the vapor pressure of liquid under pressure p' , and [318] may be said to state the effect of pressure on the vapor pressure of a liquid.

The Relation between Osmotic Pressure and Vapor Pressure

If the chamber of Fig. 218 contains a porous tube holding a solution consisting of the liquid of the pure substance as a solvent and a non-volatile solute, there will be some level S' at which the vapor and the surface of the solution will be in equilibrium. Then by [317] the solution and the vapor will be in equilibrium at all lower levels.

The chemical potential of the pure solvent in the solution at level S must be the same, for equilibrium, as that of the vapor at the same level. If the chamber contains a parallel column of pure solvent in a porous tube, the chemical potential of the pure solvent at any level will be the same as that of the surrounding vapor, which in turn is the same as that of the solvent in the solution at the same level. Therefore, if the two columns are joined at any level by a passage which is closed by a membrane permeable to the solvent but not to the solute, then the solvent and the solution will be in equilibrium through the membrane.

Let us assume that the vapor pressure of the solution is less than that of the pure solvent. Then for equilibrium the free surface of the solution will stand at some level S' which is higher than the level S of the free surface of the pure solvent. The difference between the two vapor pressures will be represented by the hydrostatic head of vapor between S and S' . If we let p_s denote the pressure of the vapor at the level S

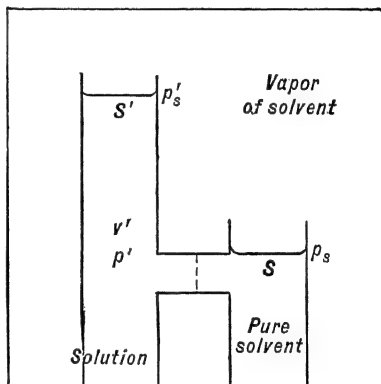


FIG. 218. Equilibrium of Solution and Solvent (Osmotic Pressure)

* If for $p' - p_s$ we substitute the capillary force per unit area $2\sigma/r$, [318] becomes identical with [250], the equation for equilibrium between a vapor and a curved surface of a liquid.

and p'_s that at level S' , we have, by [318],

$$\ln \frac{p_s}{p'_s} = \frac{v'(p' - p'_s)}{RT},$$

where p' denotes the pressure of the solution at level S , v' the specific volume of the solution, and R the gas constant for the pure vapor.

If the two columns of liquid are connected at level S through a membrane which is permeable only to the solvent, then the membrane must support the difference between the pressure of the solution p' and the pressure of the solvent p_s . This difference in pressure is called the *osmotic pressure*. It is a measure of the force necessary to prevent solvent from entering the solution to dilute it.

The osmotic pressure $(p' - p_s)$ is large compared with the difference between the two vapor pressures p_s and p'_s . Therefore we need not distinguish between the osmotic pressure and the quantity $(p' - p'_s)$ which appears in the last equation. Solving this equation, we get for the osmotic pressure

$$p' - p_s = RT \ln \frac{p_s}{p'_s}.$$

Equilibrium between a Mixture and a Pure Liquid Phase

Sometimes a single component of a mixture can condense to form a pure liquid phase in which other components of the mixture are only

slightly absorbed, as in the formation of liquid water from moist air. The condition of equilibrium can be illustrated by the container shown in Fig. 219, in which the vertical dash line denotes a membrane permeable to the vapor of substance 1 only and the hatched strip denotes a porous wall which permits the vapor of substance 1 to pass but restrains the liquid. On the right-hand side of the membrane is a mixture of substances

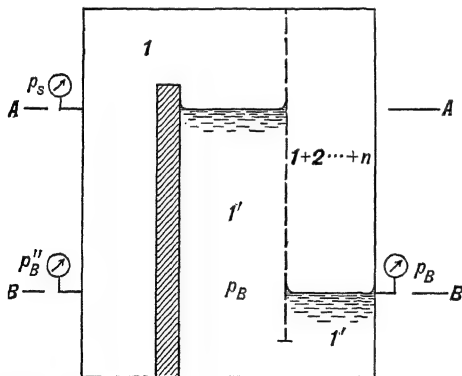


FIG. 219. Equilibrium between a Mixture and a Pure Liquid Phase

1, 2, \dots n in the vapor phase with, at the bottom, some of substance 1 in the pure liquid phase (indicated by $1'$). On the left-hand side of the membrane is substance 1 in the pure liquid phase (in-

icated by 1') and in the pure vapor phase (indicated by 1). A gap at the bottom of the membrane permits the liquid to communicate freely between the two columns.

If the Gibbs-Dalton Law holds for the mixture, the pressure of the vapor on the left-hand side of the membrane will be less than the pressure of the mixture on the right-hand side. Therefore the level of the surface of the liquid on the left must be higher than that on the right in order to balance by the hydrostatic head the difference in pressure between the two columns of vapor. The porous wall separates the left-hand column of liquid from an adjacent column of pure vapor of substance 1 which has access to the free surface of the liquid over the top of the porous wall.

First let us consider the level *AA* corresponding to the surface of the liquid exposed to its own vapor. For equilibrium, according to [280], the chemical potentials of the pure liquid, of the pure vapor, and of substance 1 in the mixture must be identical. Then by the Gibbs-Dalton Law the pressure of the mixture at level *AA* can be stated in the form

$$p = p_s + p_2 \cdots + p_n,$$

where p_s denotes the saturation pressure of substance 1 at the temperature of the system, and $p_2 \cdots p_n$ denote the partial pressures of components 2 \cdots n in the mixture. Now if the density of the mixture is small compared with the density of the liquid, this value of the pressure may be considered to be the same as that at the level of the free liquid surface *BB* in equilibrium with the mixture. In that event the partial pressure of a vapor over its own liquid is the normal saturation pressure of the vapor regardless of the number or kind of gases mixed with it.

For a more rigorous value of the partial pressure of the vapor we must study level *BB*. For equilibrium the chemical potential of the pure vapor of substance 1 must be identical with that of the pure liquid, and the chemical potential of either of these must be identical with that of substance 1 in the mixture — all at the same level. Since the chemical potential and the temperature are adequate to determine the state, it follows that the pure vapor at level *BB* having pressure p_B'' would be in equilibrium with the mixture at level *BB* if the two were connected through a semipermeable membrane. Therefore, the partial pressure p_{1B} of substance 1 in the mixture at level *BB* is p_B'' . That is, p_B'' is the partial pressure of substance 1 in a mixture which is in equilibrium with the pure liquid phase of substance 1.

To find the partial pressure of substance 1 in a mixture that is in equilibrium at pressure p_B with the liquid phase of substance 1, it is only

necessary to find the pressure of the pure vapor of substance 1 that will be in equilibrium with liquid under the pressure p_B . The expression [318] for this quantity was derived above, and in terms of the present symbols it is

$$\ln \frac{p_B''}{p_s} = \frac{(p_B - p_s)v'}{R_1 T}$$

or

$$\ln \frac{p_{1B}}{p_s} = \frac{(p_B - p_s)v'}{R_1 T} \quad [319]$$

The quantity p_{1B} as found from this equation may be included in the summation prescribed by the Gibbs-Dalton Law. Moreover, the other properties of the pure vapor at level BB may be included in the summations [312] and [313] to find the corresponding properties of the mixture at the same level.

Let us apply [319] to a mixture of air and water vapor in equilibrium with liquid water at a temperature of 100 F (560 F abs) and at a pressure of 15 lb/per sq in. abs. The gas constant for water vapor is

$$R_1 = 85.7 \text{ ft F}^{-1}.$$

Substitution gives

$$\ln \frac{p_{1B}}{p_s} = 0.0007,$$

or

$$\frac{p_{1B}}{p_s} = 1.0007;$$

that is, the partial pressure of water vapor in the mixture is 7 parts in 10,000 higher than the saturation pressure. Since

$$p_s = 0.9492 \text{ lb/sq in.},$$

then

$$p_{1B} = 0.9499 \text{ lb/sq in.}$$

For ordinary engineering purposes a difference of this magnitude may be ignored.

The Phase Rule of Gibbs

It was shown on page 461 that for any change between equilibrium states we may write for a phase of a system, if the phase is homogeneous in state,

$$S dT - V dp + m_1 d\mu_1 + m_2 d\mu_2 \cdots + m_n d\mu_n = 0. \quad [290]$$

Solving this expression for the differential of pressure, we get

$$dp = \frac{S}{V} dT + \frac{m_1}{V} d\mu_1 + \frac{m_2}{V} d\mu_2 \cdots + \frac{m_n}{V} d\mu_n. \quad [320]$$

Since the temperature and the n chemical potentials of the n components of the phase are all independent variables, it follows that

$$\begin{aligned} \left(\frac{\partial p}{\partial T} \right)_{\mu_1, \mu_2, \dots} &= \frac{S}{V}, \\ \left(\frac{\partial p}{\partial \mu_1} \right)_{T, \mu_2, \mu_3, \dots} &= \frac{m_1}{V}, \text{ etc.} \end{aligned} \quad [321]$$

Therefore, the entropy per unit volume of the phase and the concentration of each component in the phase are determined by the relation between temperature, pressure, and the chemical potentials of the components. In fact, all the other properties of the phase, except those dependent on its total mass, are determined by the same relation. For, if we write [288] in the form

$$\frac{E}{V} = T \frac{S}{V} - p + \mu_1 \frac{m_1}{V} + \mu_2 \frac{m_2}{V} + \cdots,$$

it becomes apparent that the energy per unit volume is determined by the temperature, the pressure, the chemical potentials, and the relation that exists between them. It may be easily shown that ψ/V and Z/V are similarly determined. It follows that for each homogeneous phase in a heterogeneous system there is an equation between $n + 2$ independent variables of the form

$$f(T, p, \mu_1, \mu_2, \cdots \mu_n) = 0 \quad [322]$$

which completely determines all the properties of that phase, except those dependent on its total mass.

If there are r such phases in equilibrium with each other, then there are r equations of the form [322]; namely,

$$\begin{aligned} f'(T, p, \mu_1, \mu_2, \cdots \mu_n) &= 0, \\ f''(T, p, \mu_1, \mu_2, \cdots \mu_n) &= 0, \\ \text{etc.} \end{aligned}$$

But by the conditions of equilibrium [268], [269], and [272], the values of $T, p, \mu_1, \cdots \mu_n$ must be the same in each of the r equations in which they appear, and the equations are therefore simultaneous equations in these $(n + 2)$ variables. When they are reduced there will remain

$(n + 2 - r)$ independent variables, or

$$F = n + 2 - r, \quad [323]$$

where F is the number of independent variables or "degrees of freedom." That is, F is the maximum number of phase properties which can be independently changed without changing either the number of homogeneous phases of the system or the number of possible components of the parts. The term *phase property* is used here to denote any property of any phase that is independent of the mass of the phase. Equation [323] is then the *phase rule* of Gibbs.

For example, a system which is a pure substance may have states consisting of a single phase (solid, liquid, or gaseous) or of two coexistent phases (such as solid and liquid or liquid and gaseous) or of three coexistent phases (such as solid, liquid, and gaseous at the triple point). For the single phase, by [323], F is 2; therefore, the temperature and the pressure or, alternatively, the temperature and the chemical potential, may be varied independently without forming additional phases. For two coexisting phases F is 1; therefore, only the temperature (or the pressure, or the chemical potential of either phase) may be changed without changing the number of phases. If the pressure is changed, the temperature changes in accordance with the pressure-temperature relation at saturation, but the temperature cannot be changed independently without causing one of the phases to vanish. For three coexisting phases F is zero; therefore, none of the properties pressure, temperature, or chemical potential can be changed without changing the number of phases. For all possible three-phase states of the system the pressure must be the same, the temperature must be the same, and the chemical potential must be the same.

As a more complex case consider a solution of NaCl in water. If the system is entirely in the liquid phase then

$$F = 2 + 2 - 1 = 3.$$

That is, the pressure, the temperature, and the concentration of the salt, on which its chemical potential depends, can all be varied independently without the formation of a new phase. When solid salt is in equilibrium with the solution, r is 2 and F reduces to 2. Then the pressure and temperature may be independently varied, but for each combination of the two there is a corresponding concentration of salt in the solution. Such a solution is called a *saturated solution*. When solid salt is in equilibrium with a solution which is in turn in equilibrium with vapor from the solution, F is 1. Then for each value of the temperature the pressure is the vapor pressure of a saturated solution at that tempera-

ture, and the concentration of the salt is that corresponding to saturation. Thus pressure and concentration are no longer independent of temperature.

Properties of a Surface of Discontinuity between a Liquid and Its Vapor

Consider a spherical drop of liquid that is exposed to an atmosphere of its own vapor (Fig. 220). Let us assume that this drop consists of a large central core of liquid, homogeneous in state, which is surrounded by a thin film of the same material in some "surface state." If we signify the liquid phase by $'$ and the vapor phase by $''$, we may write for each the equations [261], [288], and [280]:

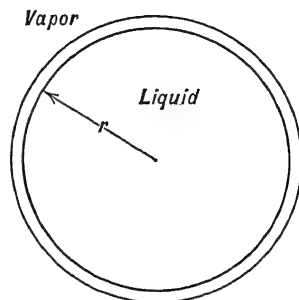


FIG. 220

$$dE' = T dS' - p' dV' + \mu' dm',$$

$$dE'' = T dS'' - p'' dV'' + \mu'' dm'',$$

$$E' = TS' - p'V' + \mu'm',$$

$$E'' = TS'' - p''V'' + \mu''m''$$

$$\mu' = \zeta', \quad \text{and} \quad \mu'' = \zeta''$$

The same symbol is used for temperature in both phases, because equilibrium demands uniformity of temperature. Different symbols are used for pressure in the two phases because the characteristics of the film make uniformity of pressure unnecessary for equilibrium.

If we consider the film to occupy a negligible volume, then work can be done on it in a reversible process only by means of a change in its area. Therefore, the equation corresponding to [261] for the film is

$$dE_f = T dS_f + \sigma dF + \mu_f dm_f, \quad [324]$$

where the subscript f signifies a property of the film, F denotes the area of the surface of the film, and σ is defined by the equation

$$\sigma = \left(\frac{\partial E}{\partial F} \right)_{S_f, m_f}.$$

It is now easy to show that the equation corresponding to [288] is

$$E_f = TS_f + \sigma F + \mu_f m_f, \quad [325]$$

from which we get

$$\mu_f = e_f - Ts_f - \sigma f,$$

where the lower-case symbols denote values of the corresponding properties per unit mass of film.

Equilibrium of Forces

Let us assume the entire system consisting of liquid, vapor, and film to be enclosed in a container of invariable volume. As a test for equilibrium suppose that the volume of the liquid drop increases so that its surface increases and the volume of the vapor decreases, but without any exchange of material between either pure phase and the film. Then the variation in energy of the system as a whole is

$$\begin{aligned}\delta E &= \delta E' + \delta E'' + \delta E_f \\ &= T \delta S' - p' \delta V' + T \delta S'' - p'' \delta V'' + T \delta S_f + \sigma \delta F \\ &= T \delta S - p' \delta V' - p'' \delta V'' + \sigma \delta F,\end{aligned}$$

where δS denotes the increase in entropy of the system as a whole. If this variation occurs at constant entropy ($T \delta S = 0$), then for equilibrium the energy of the system must not decrease: that is,

$$\sigma \delta F - p' \delta V' - p'' \delta V'' \geq 0.$$

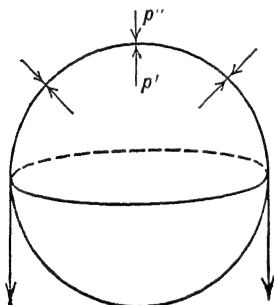


FIG. 221

In this last equation only the equality can hold because the reverse variation is also possible. Noting that the volume of the entire system is unchanged by the variation, we may write

$$\sigma \delta F = (p' - p'') \delta V, \quad [326]$$

where δV denotes the increase in the volume of the drop and also the decrease in the volume of the vapor if the change in volume of the film can be neglected. The expressions for the surface and the volume of a sphere in terms of its radius are respectively

$$F = 4\pi r^2$$

and

$$V = \frac{4}{3}\pi r^3.$$

Therefore $dV/dF = r/2$, and, from [326],

$$\sigma = \frac{1}{2}(p' - p'')r. \quad [327]$$

Consider a liquid, homogeneous in state, contained in a spherical membrane of uniform tension α per unit length (Fig. 221). For dynamic equilibrium the tension of the membrane along a great circle must balance

the normal components of the pressures on a hemisphere. That is,

$$2\pi r\alpha = \pi r^2(p' - p''),$$

where p' denotes the internal pressure and p'' the external pressure. It follows that

$$\alpha = \frac{1}{2}(p' - p'')r,$$

which is the same as the expression given above for the differential coefficient σ . By virtue of this analogy σ is known as the "surface tension."

Equilibrium of Masses

As a second test for equilibrium suppose that a mass δm transfers from the liquid phase to the surface film while the entropy of the whole system, the volume of each part, and the surface area of the film are kept constant. Since the vapor phase is unaffected,

$$\begin{aligned}\delta E &= T \delta S' - \mu' \delta m + T \delta S_f + \mu_f \delta m \\ &= T \delta S + (\mu_f - \mu') \delta m.\end{aligned}$$

By assumption $\delta S = 0$, and for equilibrium $\delta E \geq 0$. Therefore,

$$(\mu_f - \mu') \delta m \geq 0.$$

Only the equality will hold since the variation can occur in either direction. Therefore, for equilibrium

$$\mu_f = \mu' = \zeta'$$

by [280]. Similarly it can be shown that

$$\mu_f = \mu'' = \zeta''.$$

Therefore,

$$\mu_f = \zeta' = \zeta''. \quad [328]$$

Instability of the Drop

The variations discussed above disclose no instability. However, the discussion on page 437 shows that equilibrium between a drop of liquid and surrounding vapor is unstable. The following considerations confirm this conclusion.

For the state of equilibrium we have

$$\mu' = \mu'', \text{ or } \zeta' = \zeta''.$$

Consider a variation at constant temperature for which a small amount of fluid transfers from the drop to the surrounding vapor. The result will be a decrease in the radius of the drop. If the vapor surrounding the drop is sufficiently extensive the effect of the variation on its pressure

will be negligible. The pressure in the drop, however, will increase with decrease in the size of the drop in accordance with [252]. At constant temperature

$$d\xi' = v' dp',$$

so that ξ' will be greater than ξ'' after the variation.

The result of this variation is to increase the escaping tendency of the material within the drop without altering the escaping tendency of the surrounding vapor. Therefore, evaporation will proceed further, once it starts. Similarly it may be shown that condensation will proceed further, once it starts. Equilibrium between the drop and its environment is therefore unstable.

The Kelvin-Helmholtz Relation

A permeable film between the liquid phase and the vapor phase is like the porous wall described on page 471 in that it can support a difference in pressure between two phases in equilibrium. Therefore the relation [318] between the pressure of a liquid and its vapor will hold. If we substitute for $(p' - p_s)$ in [318] the expression for its approximate equivalent $(p' - p'')$ from [327], we get the Kelvin-Helmholtz relation

$$\ln \frac{p''}{p_s} = \frac{2\sigma v'}{rRT} \quad [250]$$

The Change in Surface Tension with Temperature and with Pressure Difference

The pressure of the vapor and of the liquid are independently variable. However, the difference between the pressures of the vapor and the liquid is fixed according to [327] by the surface tension and the radius of curvature. When this difference vanishes the surface is plane. We shall find the variation in surface tension with this difference in pressure and with temperature.

If we differentiate [325] and simplify with the aid of [324] we get

$$S_f dT + F d\sigma + m_f d\mu_f = 0, \quad [329]$$

from which we get

$$d\mu_f = -\frac{S_f}{m_f} dT - \frac{F}{m_f} d\sigma. \quad [330]$$

For the liquid phase and for the vapor phase we may write [290]

$$\begin{aligned} S' dT - V' dp' + m' d\mu' &= 0, \\ S'' dT - V'' dp'' + m'' d\mu'' &= 0. \end{aligned}$$

Solving each of these for the differential of pressure and taking the difference, we have

$$d(p' - p'') = dp' - dp'' = \left(\frac{S'}{V'} - \frac{S''}{V''} \right) dT + \left(\frac{1}{v'} - \frac{1}{v''} \right) d\mu,$$

where

$$\mu = \mu' = \mu''$$

Solving for $d\mu$, we get

$$d\mu = \frac{1}{(1/v' - 1/v'')} \left[d(p' - p'') + \left(\frac{S''}{V''} - \frac{S'}{V'} \right) dT \right]. \quad [331]$$

For any change between states of equilibrium

$$d\mu = d\mu_f.$$

Therefore, we may equate the right-hand members of [331] and [330]:

$$\left(\frac{1}{1/v' - 1/v''} \right) \left[d(p' - p'') + \left(\frac{S''}{V''} - \frac{S'}{V'} \right) dT \right] = \frac{1}{m_f} (-S_f dT - F d\sigma).$$

Solving for $d\sigma$, we have

$$d\sigma = - \left[\frac{S_f}{F} + \frac{m_f}{F(1/v' - 1/v'')} \left(\frac{S''}{V''} - \frac{S'}{V'} \right) \right] dT \\ - \frac{1}{F(1/v' - 1/v'')} d(p' - p'').$$

The differential coefficient with respect to temperature is therefore

$$\left(\frac{\partial \sigma}{\partial T} \right)_{(p' - p'')} = - \left[\frac{S_f}{F} + \frac{m_f}{F(1/v' - 1/v'')} \left(\frac{S''}{V''} - \frac{S'}{V'} \right) \right], \quad [332]$$

and that with respect to the difference in pressure is

$$\left[\frac{\partial \sigma}{\partial (p' - p'')} \right]_T = - \frac{m_f}{F(1/v' - 1/v'')}. \quad [333]$$

The right-hand member of this equation has a certain significance if the density of the vapor ($1/v''$) is negligible compared with that of the liquid ($1/v'$). For then the quantity $m_f/F(1/v' - 1/v'')$ becomes the thickness the film would have if its density were identical with that of the liquid phase. This is doubtless a very minute quantity — of the order of magnitude of the diameter of a molecule. It is therefore probable that for surfaces that are nearly plane [332] may be approximated by the equation

$$\left(\frac{\partial \sigma}{\partial T} \right)_{(p' - p'')} = - \frac{S_f}{F}. \quad [332a]$$

The Energy of the Film

The energy of the film per unit area of its surface is found from [325] to be

$$\frac{E}{F} = T \frac{S_f}{F} + \sigma + \mu_f \frac{m_f}{F}.$$

The last term in this expression must be very small since (m_f/F) is the mass of the film per unit area. Neglecting this term and substituting from [332a], we get

$$\frac{E}{F} = \sigma - T \left(\frac{\partial \sigma}{\partial T} \right)_{(p'-p'')}. \quad [334]$$

This is an expression that is frequently employed. It may be derived by other methods* for the energy of a plane stretched membrane which is impermeable to and distinct from the material in the contiguous phases.

PROBLEMS

1. Starting from the conditions of equilibrium of a heterogeneous system, show that equilibrium will subsist (in the absence of membranes impermeable to any substance) only if the pressure of the system is uniform.

2. Consider a system consisting of a pure substance in an equilibrium state consisting of three phases (a triple-point state). From the conditions of equilibrium for a heterogeneous system as developed in this chapter, state the conditions of equilibrium for the pure substance in the absence of gravity, electricity, magnetism, and capillarity. Compare these conclusions with those of Chapter XXIV.

3. (a) Plot the escaping tendency, in terms of the chemical potential, against temperature for saturated liquid water.

(b) Plot the same quantity against pressures ranging from 5000 to 1 lb/sq in. abs for a temperature of 500 F.

(c) Plot the same quantity against temperatures ranging from 32 to 1000 F for a pressure of 500 lb/sq in. abs.

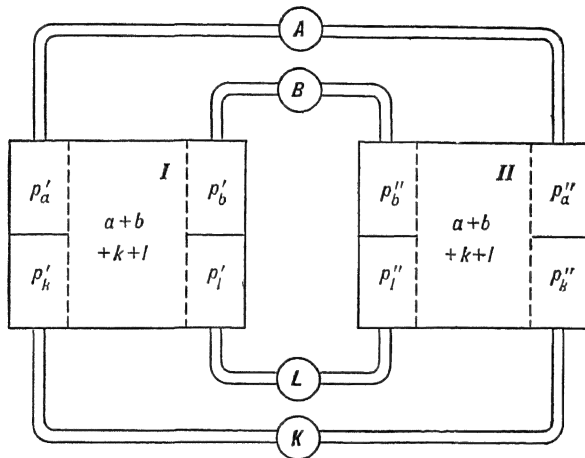
4. (a) The boiling point of water is raised 0.513 C per gram mole of a non-volatile solute in each kilogram of water. Find the value of the chemical potential of water in a solution of 3 moles of NaCl in a kilogram of water at the boiling point of the solution at a pressure of 1 atmosphere.

(b) Assuming that the effect on the boiling point is the same for various pressures near atmospheric pressure, compare values of the chemical potential for pure water and for the salt solution, both at 100 C and both at their respective boiling pressures.

* Hoare, *Thermodynamics*, Longmans, 1931, p. 195. Rice, *Commentary on the Scientific Writings of J. W. Gibbs*, Yale University Press, 1936, Vol. 1, p. 588.

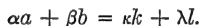
5. It was shown in Chapter XIV that the decrease in Z at constant pressure and temperature is the maximum possible work that can be realized from a chemical reaction. Discuss the relationship between this fact and the fact that for equilibrium the value of K_p is fixed by the temperature.

6. The sketch shows two boxes I and II in each of which the substances a , b , k , and l are in chemical equilibrium at the same temperature T . The pure substance a at the pressure p'_a is in equilibrium through a semipermeable membrane with the composite system in box I. The pure substance a at the pressure p''_a is in equilibrium with the composite system in box II.



(a) Find an expression for the work that would be delivered in a reversible isothermal steady-flow expansion through engine A from p'_a to p''_a per mole of substance a . Assume a to be a perfect gas, and give the expression in terms of the temperature and the pressures.

The substances a , b , k , and l react in accordance with the chemical equation



If the substances a and b flow into either box in the proportions $\alpha : \beta$, and the substances k and l flow out in the proportions $\kappa : \lambda$, no change in the state of fluid in the box will be observable if the mass flow in is equal to the mass flow out. Moreover, since the substances in the box are in chemical equilibrium the flow could occur in either direction.

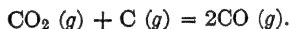
(b) Find an expression for the net work of engines A , B , K , and L .

Note that all operations in this steady-flow cycle are isothermal and reversible.

(c) What must be the magnitude of the net work?

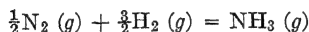
(d) Compare the result of conclusion (c) with the condition for equilibrium in terms of K_p .

7. (a) From Fig. 212 find the value of K_p at 900 K for the reaction



- (b) Calculate the corresponding values of K_c and K_p .
 (c) Find the per cent of CO that dissociates into C and CO₂ at this temperature at a pressure of 1 atmosphere.
 (d) If the pressure is increased will a larger or a smaller fraction dissociate?

8. Answer questions (a) to (d) from the preceding problem for the reaction



at 400 K.

(e) If an inert gas, such as helium, is added to the mixture without changing its total pressure, would a larger or smaller fraction of NH₃ dissociate?

9. From Fig. 212 find the degree of dissociation of water vapor at 2000 K.

10. (a) Find an expression for y in the definition of fugacity,

$$RT \ln f = \mu - y,$$

such that at very low pressures the fugacity and the pressure are identical:

(b) Plot to the same scale of ordinates against temperature as abscissa values of the fugacity and the pressure for all saturation states of liquid and vapor water between 32 F and the critical temperature.

11. Raoult's Law states that the partial pressure p'_s of the vapor of a solvent in equilibrium with a solution is given by

$$p'_s = xp_s$$

where p_s denotes the vapor pressure of the pure solvent and x the mole fraction of the solvent in the solution.

(a) Derive an expression for the osmotic pressure of such a solution in terms of x , the temperature, and the specific volume of the solution.

(b) An osmotic pressure of 36.7 cm Hg has been observed for a solution which contains 0.00199 g of glycerine per g of solution at a temperature of 0 C. Compare this with the corresponding value from Raoult's Law.

12. At a temperature of 100 F how much water would be required to saturate 1 cu ft of air if the total pressure of the air and water vapor is 3000 lb/sq in. abs? Compare this with the amount required to saturate the same volume of air at 15 lb/sq in. abs.

13. Find an expression for the maximum number of coexistent phases for mixtures of various numbers of components. What is the maximum number of coexistent phases for a binary mixture and for a ternary mixture?

SYMBOLS

$a, b \dots k, l \dots$	units of corresponding substance
c	concentration
c_p	specific heat at constant pressure
D	a positive number

E	internal energy of a system
f	fugacity
F	number of independent variables, area of surface
m	mass
M	chemical potential for an actual component
p	pressure
R	gas constant
R	universal gas constant
S	entropy
T	absolute temperature
v	specific volume
v_g	specific volume of saturated vapor
V	volume
W	work from system
x	mole fraction
y	vertical distance, function of temperature
Y	function of temperature

GREEK LETTERS

$\alpha, \beta, \dots, \kappa, \lambda, \dots$	numbers
α	tension per unit length
δ	variation in property (first order)
ϵ	fraction of substance dissociated
μ	chemical potential
ρ	density in moles per unit volume
σ	surface tension
ζ	$(u + pv - Ts)$

SUBSCRIPTS

c	concentration
m	mixture
m_1, m_2, \dots	constant mass of substance 1, 2, \dots
p	constant pressure
s	surface
S	constant entropy, level, solvent
V	constant volume

SUPERSCRIPTS

$'$, $''$, $'''$	used to distinguish properties of various phases
$'$	liquid
$''$	vapor

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